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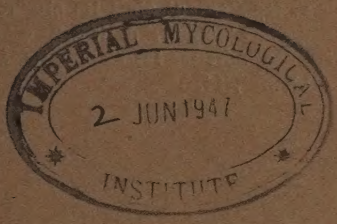

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MATHÉMATIQUES

SUR LES NOMBRES DE LA FORME $a^m \pm b^m$

Par A. A. KULAKOFF

(Présenté par S. L. Soboleff, de l'Académie, le 25.III.1943)

Dans mon travail: «Sur quelques propriétés des nombres de la forme $a^m + b^m$» (1)* ont été demontrés des divers théorèmes concernant le plus grand commun diviseur des nombres $a^m \pm b^m$ et $a^n \pm b^n$, où a, b, m et n sont des nombres naturels. Dans le § 1 du présent article nous démontrons quelques théorèmes ultérieurs sur les nombres de la forme ci-dessus indiquée. Dans les paragraphes suivants sont établies des diverses conditions nécessaires pour que l'équation bien-connue de Fermat soit résoluble en nombres naturels, ainsi que quelques généralisations de certains théorèmes de la théorie élémentaire des nombres.

§ 1. Soient a, b, m et n des nombres naturels, m étant pair, et $ab \neq 1$. Admettons d'ailleurs que $(a, b) = (m, n) = 1$. Alors $d_1 = (a^m + b^m, a^n + b^n)$ divise 2**.

En effet, d_1 divise l'un au moins des nombres $a + b$ et $a - b$ (P., § 1), donc d_1 divise $a^2 - b^2$. Or, $a^m - b^m$ est divisible par $a^2 - b^2$, donc $d_1' = (a^m + b^m, a^m - b^m)$ est divisible par d_1, ce qui démontre notre assertion, puisque d_1' divise 2.

Soient a et b des nombres naturels définis comme plus haut et p un nombre premier impair. Alors $d_2 = (a^p - b^p, a^r + b^r)$ divise 2 quel que soit le nombre naturel r.

Cela est clair, si r est divisible par p, puisque dans ce cas d_2 divise $(a^r - b^r, a^r + b^r)$. Si p ne divise pas r, nous avons $(r, p) = 1$, donc d_2 divise 2 en vertu d'un théorème démontré dans P. (§ 1).

En se servant des raisonnements analogues on peur démontrer aussi que $d_3 = (a^p + b^p, a^s - b^s)$, où p est un nombre premier $\geqslant 2$ et s est un nombre naturel impair quelconque, divise 2.

Il est à remarquer encore que les résultats ci-dessus établis se laissent un peu préciser. On s'aperçoit notamment sans peine que chacun des nombres d_1, d_2 et d_3 est égal à 2 ou à 1 suivant que les nombres a et b sont de la meme parité ou non.

§ 2. En s'appuyant sur quelques-uns des résultats du paragraphe précédent on peut démontrer le théorème suivant:

Pour que

$$a^p + b^p = c^p, \tag{1}$$

où p est un nombre premier impair, a et b sont des nombres naturels im-

* Nous allons désigner ce travail dans ce qui suit simplement par P.
** Dans le cas où $a = b = 1$ l'exactitude de l'assertion analogue est évidente.

pairs distincts de 1*, c est un nombre naturel pair, et $(a, b)=(a, c)=(b, c)=1$, il faut que les conditions suivantes soient vérifiées:

1) $(a, c^r+b^r)=(b, c^r+a^r)=1$ quel que soit le nombre naturel r;

2) $(c, a^s-b^s)=2$ quel que soit le nombre naturel impair s.

En effet, si (1) avait lieu, c^p-b^p serait divisible par a, et par conséquent $(c_p-b^p,\ c^r+b^r)$ serait divisible par (a, c^r+b^r). Or, $(c^p-b^p,\ c^r+b^r)=1$ (§1), donc $(a, c^r+b^r)=1$.

On démontre d'une manière analogue que (1) entraîne $(b, c^r+a^r)=1$.

Remarquons enfin que (1) ne peut avoir lieu que si c divise a^p+b^p. Or, si cette condition est satisfaite, (c, a^s-b^s) divise $(a^p+b^p,\ a^s-b^s)=2$ (§ 1). D'autre part, (c, a^s-b^s) est divisible par 2, donc $(c, a^s-b^s)=2$.

On déduit aisément de ce théorème la proposition suivante. Soient a, b et c des nombres naturels définis comme plus haut et q un diviseur premier quelconque de a; si $\left(\frac{b}{q}\right) \not\equiv \left(\frac{c}{q}\right)$, alors l'égalité $a^p+b^p=c^p$ est impossible quel que soit le nombre premier impair p.

En effet, nous avons

$$\left(\frac{b}{q}\right) \equiv b^{\frac{q-1}{2}} \pmod q \quad \text{et} \quad \left(\frac{c}{q}\right) \equiv c^{\frac{q-1}{2}} \pmod q,$$

d'où il suit:

$$b^{\frac{q-1}{2}}+c^{\frac{q-1}{2}} \equiv \left(\frac{b}{q}\right)+\left(\frac{c}{q}\right)=0 \pmod q.$$

Par conséquent, $(b^{\frac{q-1}{2}}+c^{\frac{q-1}{2}},\ a) \neq 1$, d'où résulte notre assertion.

On obtient un résultat analogue dans le cas où $\left(\frac{a}{q_1}\right) \not\equiv \left(\frac{c}{q_1}\right)$, q_1 étant un diviseur premier de b.

§ 3. Soient a, b et k des nombres naturels premiers entre eux deux à deux, et $ab \neq 1$. Supposons que a^m-b^m et a^n-b^n, où m et n sont des nombres naturels, soient divisibles par k, n étant le plus petit nombre naturel pour lequel a lieu la congruence $a^n \equiv b^n \pmod k$. Nous allons démontrer que n divise m.

En effet, si m n'était pas divisible par n, on aurait $(m, n)<n$. Chacun des nombres a^m-b^m et a^n-b^n étant divisible par k, il en serait de même de $(a^m-b^m,\ a^n-b^n)=a^{(m,n)}-b^{(m,n)}$, où $(m, n)<n$ (voir P., § 1), contrairement à notre hypothèse.

En posant $b=1$ nous retrouvons le théorème bien connu concernant les nombres appartenant à l'exposant $n \pmod k$.

On peut démontrer un théorème analogue pour les nombres a^m+b^m et a^n+b^n. Supposons notamment que les nombres soient divisibles par k et que k ne divise pas $a^{n-i}+b^{n-i}$ $(i=1, 2, \ldots, n-1)$. Alors n divise m.

Si $n=1$, le théorème est évidemment vrai. Soit maintenant $n>1$. Il est clair que dans ce cas on a $k>2$. Si n ne divisait pas m, on aurait $\delta=(m, n)<n$. Remarquons maintenant que $d_4=(a^m+b^m,\ a^n+b^n)$ est divisible par k. D'après un théorème de P. (§ 1), d_4 divise l'un au moins des nombres $a^\delta+b^\delta$ et $a^\delta-b^\delta$, donc l'un de ces nombres est divisible par k. Or, δ étant plus petit que n, c'est le nombre $a^\delta-b^\delta$ qui est divisible par k. Il en résulte qu'aussi a^m-b^m et, par suite, $d_5=(a^m+b^m,\ a^m-b^m)$ est divisible par $k>2$, ce qui est impossible, puisque d_5 divise 2. Le théorème est donc démontré.

§ 4. Soient a et b deux nombres naturels premiers entre eux dont l'un au moins est distinct de 1, et q un nombre premier impair qui ne divise pas ab. Désignons par g une racine primitive de q; admettons que $a \equiv g^{\mu_1} \pmod q$,

---

* La condition $a>1$, $b>1$ ne constitue aucune restriction essentielle, puisque (1) est évidemment impossible, si l'un au moins des nombres a et b est égal à 1.

$b \equiv g^{\mu_2} \pmod{q}$, μ_1 et μ_2 étant des nombres entiers non négatifs, et posons $d = \left(\mu_1 - \mu_2, \frac{q-1}{2}\right)$. Alors a lieu le théorème suivant:

Le nombre $a^t + b^t$ est divisible par q, pour un certain t naturel, dans le cas et dans ce cas seulement où $\frac{\mu_1 - \mu_2}{d}$ est un nombre impair.

En effet, comme $a \equiv g^{\mu_1}$, $b \equiv g^{\mu_2}$, on a

$$a^t + b^t \equiv g^{\mu_1 t} + g^{\mu_2 t} = g^{\mu_2 t}\left[g^{(\mu_1 - \mu_2)t} + 1\right],$$

en supposant que $\mu_1 > \mu_2$*. Si donc $a^t + b^t$ est divisible par q, il en est de même de $g^{(\mu_1 - \mu_2)t} + 1$, puisque $(g, q) = 1$. L'exactitude de l'assertion inverse est évidente. Tout revient donc à établir que la condition formulée ci-dessus est aussi nécessaire et suffisante pour que $g^{(\mu_1 - \mu_2)t} + 1$ soit divisible par q.

Supposons que $\frac{\mu_1 - \mu_2}{d}$ soit impair. Le nombre $g^{\frac{q-1}{2}} + 1$ est divisible par q, car g est une racine primitive de q. Il en résulte qu'aussi $g^{\frac{(\mu_1 - \mu_2)(q-1)}{2d}} + 1$ est divisible par q, ce qui montre que la condition indiquée est suffisante.

Nous allons démontrer que cette condition est en même temps nécessaire. Admettons que $g^{(\mu_1 - \mu_2)t} + 1$ soit divisible par q. Il est aisé de voir que $\frac{q-1}{2}$ est la plus petite valeur positive de τ pour laquelle $g^\tau + 1$ est divisible par q. En effet, si $g^\tau \equiv -1 \pmod{q}$ et $\tau < \frac{q-1}{2}$, alors $g^{2\tau} \equiv 1 \pmod{q}$ $(2\tau < q - 1)$, ce qui ne peut être. On en déduit que $\frac{q-1}{2}$ divise $(\mu_2 - \mu_2)t$ (§ 3) en sorte que

$$\frac{(\mu_1 - \mu_2)t}{\frac{q-1}{2}} = \frac{\frac{\mu_1 - \mu_2}{d}t}{\frac{q-1}{2d}} = v,$$

où v est un nombre naturel. On voit donc que t est divisible par $\frac{q-1}{2d}$, d'où il suit que v est divisible par $\frac{\mu_1 - \mu_2}{d}$. Il en résulte que $\frac{\mu_1 - \mu_2}{d}$ doit être impair. En effet, dans le cas contraire $v = \frac{(\mu_1 - \mu_2)t}{\frac{q-1}{2}}$ serait pair, donc $(\mu_1 - \mu_2)t$ serait divisible par $q - 1$. Par conséquent, $g^{(\mu_1 - \mu_2)t} - 1$ serait divisible par $g^{q-1} - 1$ et, à plus forte raison, par q. Or, q divise aussi $g^{(\mu_1 - \mu_2)t} + 1$, donc $(g^{(\mu_1 - \mu_2)t} + 1,\ g^{((\mu_1 - \mu_2)t} - 1)$ serait divisible par $q > 2$, ce qui est impossible. Le théorème est donc démontré.

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LITTÉRATURE CITÉE

[1] A. Kulakoff, L'Enseignement mathématique, 37, No. 1—2, 73 (1938).

* Si $\mu_1 = \mu_2$, alors q divise $a - b$ et, par suite, ne divise pas $a^t + b^t$, puisque $(a - b,\ a^t + b^t)$ divise 2.

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MATHEMATICS

ON THE PROBLEM OF HERMITE-HURWITZ FOR INTEGER TRANSCENDENTAL FUNCTIONS

By N. MEYMANN

(Communicated by S. L. Soboleff, Member of the Academy, 3.IV. 1943)

1°. In this paper conditions are investigated under which all roots of an integer function lie in the open upper half-plane. In particular, the results of N. Tschebotarëw ([5-7]) and L. Pontrjagin ([4]) are generalized.

2°. We write an integer function $F(z)$ in the form

$$F(z)=g(z)+ih(z),$$

where $g(z)$, $h(z)$ are integer functions with real coefficients. We suppose that $g(z)$ and $h(z)$ have no common roots.

Definition 1. An intiger function which has no roots in the lower half-plane will be called H-function.

Definition 2. An integer function will be called a function of the class B, if for each $\varepsilon>0$ the inequality

$$\left|\frac{F(z)}{\overline{F}(z)}\right|<e^{\varepsilon|z|} \tag{1}$$

holds for all values of z which lie in the upper half-plane, $|z|$ being sufficiently large. By $\overline{F}(z)$ we denote $g(z)-ih(z)$.

Note. If $F(z)\in B$, then $F(z)$ can have only a finite number of roots in the upper half-plane. We can prove, by applying Phragmen-Lindelöf's theorem, that from (1) follows

$$\left|\frac{F(z)}{\overline{F}(z)}\right|<1+\eta \tag{2}$$

any $\eta>0$, z lying in the upper half-plane and $|z|$ being sufficiently large.

Definition 3. The intersection of the classes B and H will be denoted by $\overline{B}$. In virtue of Phragmen-Lindelöf's theorem the class $\overline{B}$ coincides with the totality of integer functions which satisfy the inequality

$$\left|\frac{F(z)}{\overline{F}(z)}\right|<1 \tag{3}$$

in the whole upper half-plane.

Definition 4. According to N. Tschebotarëw's paper ([6]), we shall say: two real functions $u(z)$, $v(z)$ without common roots form a real couple if for any real λ, μ the function $\lambda u(z)+\mu v(z)$ has no imaginary roots.

It is evident that the series $\sum J\frac{1}{z_\nu}$, where z_ν are the zeroes of a function of the class B, is convergent in virtue of a theorem by Blaschke (1).

Theorem 1. If $F(z)\in\overline{B}$, *then the function* $F_\varepsilon(z)=g(z)+(i+\varepsilon)h(z)$ *is also contained in* $\overline{B}$ *for any imaginary* ε *where* $|\varepsilon|<1$.

Proof. Since $\left|\frac{g(z)+ih(z)}{g(z)-ih(z)}\right|<1$ for $Jz>0$ we have $J\frac{g(z)}{h(z)}:Jz<0$ and, consequently, $\left|\frac{\frac{g(z)}{h(z)}+i+\varepsilon}{\frac{g(z)}{h(z)}-i+\bar{\varepsilon}}\right|<1$ for $Jz>0$, $|\varepsilon|<1$. Thus, $F_\varepsilon(z)$ satisfies (3), q. e. d.

Theorem 2. *If for sufficiently small* $|\varepsilon|$ *the function* $F_\varepsilon(z)$ *has no zeroes in the lower half-plane, we have* $F(z)\in\overline{B}$.

Proof. According to the condition, the quotient $\frac{g(s)}{h(z)}$ for $Jz>0$ takes no values lying within a certain circle having its centre at i. Therefore there exists a constant C such that

$$\left|\frac{\frac{g(z)}{h(z)}+i}{\frac{g(z)}{h(z)}-i}\right|<C \text{ for } Jz>0.$$

Theorem 3. *If* $F(z)\in\overline{B}$, *then* $g(z)$ *and* $h(z)$ *form a real couple, and therefore* $J\frac{g(z)}{h(z)}:Jz<0$. *Conversely, if this inequality is satisfied,* $g(z)$ *and* $h(z)$ *form a real couple, and* $F(z)\in\overline{B}$.

Proof. If $F(z)\in\overline{B}$, then, in virtue of (3), $J\frac{g(z)}{h(z)}<0$ holds for each point of the open upper half-plane. Therefore, the quotient $\frac{g(z)}{h(z)}$ can take no real values for imaginary values of z.

3°. For families of functions for which the classes H and B coincide (i. e. for families, within which $f\in H$ implies $f\in B$), the problem of Hermite-Hurwitz can easily be reduced to the behaviour of $g(z)$ and $h(z)$ on the real axis and to the absence of imaginary roots. The foregoing papers were devoted to the solution of the problem only for such families.

Integer functions of order <1 and functions of the form $F(z)=\sum_{lk=0}^{n}C_{lk}z^l e^{i\alpha_k z}$; where $\alpha\geqslant 0$, are examples of such families.

4°. A question arises: under what conditions $F(z)$ belongs to $\overline{B}$?

Theorem 4. *If* $F(z)=g(z)+ih(z)\in\overline{B}$, *then* $g(z)$ *and* $h(z)$ *have no imaginary roots, and the argument of* $F(z)$ *monotonously increases along the real axis; its derivative in regard of* x $(z=x+iy)$ *remains everywhere positive:*

$$\frac{h'(x)\,g(x)-g'(x)\,h(x)}{h^2(x)+g^2(x)}>0. \qquad (4)$$

Proof. At the points for which either $g(z)$ or $h(z)$ is zero, we have $\frac{F(z)}{\overline{F}(z)}=\pm 1$, which contradicts (3). The monotonous increase of $\arg F(z)$ along the x-axis is a consequence of the fact that the function $\zeta(z)=\frac{F(z)}{\overline{F}(z)}$ so maps the upper half-plane onto the circle $|\zeta|\leqslant 1$ that the real axis changes into a circumference $|\zeta|=1$ repeated some finite or infinite number of times. Since the angles are conservated on a conform mapping, the direction of the motion along the circle is always positive.

It follows from the monotonous increase of arg $F(z)$ that the roots of $g(z)$ and $h(z)$ interlace.

Corollary. If $g(z)$ and $h(z)$ form a real couple, then all their roots are real, simple and interlacing.

The conditions of Theorem 4 are surely not sufficient in order that $F(z)\in\overline{B}$ and neither necessary nor sufficient for $F(z)\in H$. However, as is shown below, these conditions are necessary and sufficient in order that a function of the class B belong to the class H.

Theorem 5. *In order that an integer function $F(z)=g(z)+ih(z)$ belong to the class $\overline{B}$, it is necessary and sufficient that the functions $g(z)$ and $h(z)$ be representable in the form*

$$\left.\begin{aligned} g(z) &= Ae^{g_1(z)}(z-a_0)\prod_1^\infty\left(1-\frac{z}{a_\nu}\right)e^{p_\nu\left(\frac{z}{a_\nu}\right)} \\ h(z) &= Be^{h_1(z)}(z-b_0)\prod_1^\infty\left(1-\frac{z}{b_\nu}\right)e^{p_\nu\left(\frac{z}{b_\nu}\right)} \end{aligned}\right\} \tag{5}$$

where the constants A, B have the same sign, all roots of $g(z)$ and $h(z)$ are real and interlacing, a_0 is the absolutely least root of $g(z)$, b_0 is the next root of $h(z)$ to the right-hand side of a_0, $g_1(z)$ and $h_1(z)$ are real integer functions, the p_ν are Weierstrass' exponents, and

$$f(z)=g_1(s)-h_1(z)+\sum_{\nu=1}^{\infty}\left[p_\nu\left(\frac{z}{a_\nu}\right)-p_\nu\left(\frac{z}{b_\nu}\right)\right]\equiv 0. \tag{6}$$

Proof. The conditions are sufficient. For, since the roots of $g(z)$ and $g(z)$ interlace, the product

$$\varphi(z)=\frac{A}{B}\,\frac{z-a_0}{z-b_0}\prod_1^\infty\frac{1-\frac{z}{a_\nu}}{1-\frac{z}{b_\nu}} \tag{7}$$

is convergent, and the series (6) represents an integer function. It is easy to show that $J\varphi(z):Jz<0$. Since, in virtue of (6), $\varphi(z)=\frac{g(z)}{h(z)}$, it follows from Theorem 3 that $F(z)\in\overline{B}$.

The Conditions are Necessary. In order to prove this, it suffices, in virtue of Theorem 4, to show that the condition (6) is necessary. Now we assume that $f(z)$ is not constant. Then $Jf(z)$ will take either all positive or all negative values in the upper half-plane. And, since $-\pi<\arg\varphi(z)<0$, the quotient

$$\frac{g(z)}{h(z)}=e^{f(z)}\varphi(z)$$

will in the upper half-plane take values with both positive and negative imaginary parts. This, however, is impossible because $F(z)\in B$.

Remark. Let $F(z)=g(z)+ih(z)$ be an integer function of finite order, and $g(z)$, $h(z)$ have only a finite number of both imaginary roots and of roots in whose vicinity arg $F(z)$ does not increase. If the condition (6) is not satisfied, then $F(z)$ has an infinite number of roots within some angle lying in the open lower half-plane.

Proof. In this case $f(z)$ is a polynomial of degree n. Then there exists a ray within an angle $\theta\leqslant\arg z\leqslant\theta+\frac{\pi}{2n}$, where $0<\theta<\frac{\pi}{2n}$, such that along this ray $e^{f(z)}$ increases more rapidly than $e^{a|z|^n}$, and another ray such

that along this ray $e^{f(z)}$ decreases more rapidly than $e^{-\alpha|z|^n}$, $\alpha > 0$. Then along these rays $\zeta(-z) = \frac{F(z)}{F(z)}$ has $+1$, resp., -1 as the asymptotic values. In virtue of Lindelöf's theorem (2), within the angle formed by these rays, $\zeta(z)$ has an infinite number of poles. Therefore, in the conjugate domain $F(z)$ has an infinite number of zeroes.

If $F(z) \in B$, then $g(z)$, $h(z)$ satisfy to the condition of the remark [Theorem I(3)]. Therefore the functions of finite order and of the class B satisfy to the condition (6).

Examples. 1. All functions of order < 1 satisfy the condition (6). Therefore, the conditions of Theorem 4 are necessary and sufficient in order that a function of order 1 belong to the class H which coincides in this case with the class $\bar{B}$.

2. Let $F(z) = \sum_{k=1}^{n} e^{i\alpha_k z} p_k(z)$, where $0 \leqslant \alpha_1 < \alpha_2 \ldots < \alpha_n$ and $p_k(z)$ are arbitrary polynomials. If $F(z) \in H$, then $F(z) \in \bar{B}$. There is no angle $\pi + \varepsilon \leqslant \arg z \leqslant 2\pi - \varepsilon$ $(0 < \varepsilon < \pi)$, where $F(z)$ has an infinity of roots. Therefore the conditions of Theorem 4 are necessary and sufficient for $F(z) \in B$ (4).

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PHYSICS

RADIOACTIVE FAMILIES

By L. B. PONIZOVSKY

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I. The systematics of isotopes assumes a more simple and logical form if, along with the usual formation of new nuclei by addition of a neutron (${}_0n^1$) and a proton (${}_1p^1$), we assume the possibility of formation of new nuclei by addition of a hypothetical particle (${}_{-1}a^1$) of unit mass and charge equal to $-e$, which may be called an aproton-type formation of nuclei.

Some regularities in the position of isotopes which are plotted on the graph (Z, A) may then be traced (1). The formation of new nuclei follows the scheme:

$$\left.\begin{array}{l} 1)\ \text{from hydrogen to oxygen } n \rightarrow p \rightarrow n \rightarrow p \rightarrow \ldots \\ 2)\ \text{from oxygen to titanium } 2n \rightarrow 2p \rightarrow 2n \rightarrow \ldots \\ 3)\ \text{from titanium to uranium } \{2n \text{ or } 4n\} \rightarrow \{2p\,(a) \text{ or } 4p\,(a)\} \rightarrow \ldots \end{array}\right\} \quad (1)$$

where n, $2n$, $4n$ denote the addition of one, two or four neutrons one after another without interruption; p, the addition of one proton; $2p\,(a)$, $4p\,(a)$, the addition of two or four protons one after another, the last of which may or may not be replaced by an aproton.

Accordingly, we call the nuclei formed by the addition of the first neutron «n-type» nuclei; by the second neutron, «$2n$-type»; by the first proton, «p-type»; by the addition of the aproton, «a-type» nuclei. The nuclei that complete the formation of a stable quartet of elementary particles, or the α-particle, we call «α-type» nuclei.

Fig. 1 shows a part of the graph (Z, A) from $Z=78$ to $Z=94$. Stable and α-active isotopes are denoted by crosses, β-active by circles and stable isotopes not yet found, but expected according to the above scheme (1), by dots. The graph shows that all known stable isotopes fit within the scheme (1). On the other hand, all nuclei which do not follow the scheme are unstable, i. e. β-active.

For elements with $Z>7$ the forbidden addition of a neutron after the first proton has been added brings us to a β-active isotope, e. g.

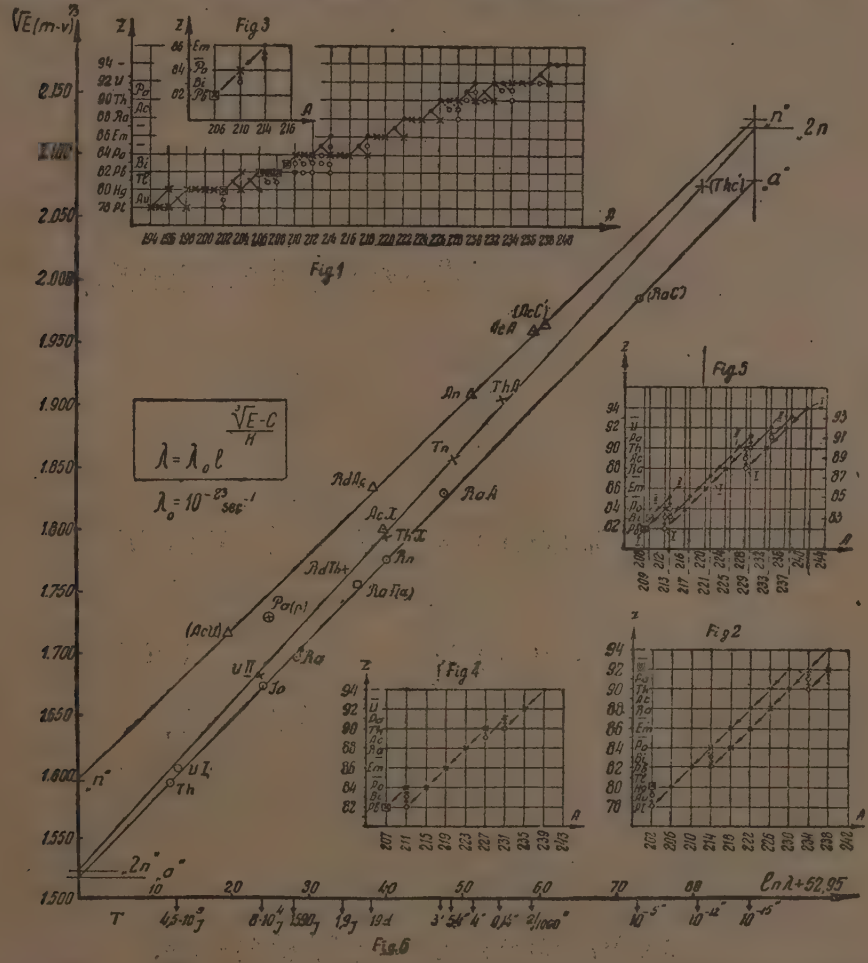
$${}_{82}Pb^{208} + {}_1p^1 = {}_{83}Bi^{209}; \quad (2) \qquad {}_{83}Bi^{209} + {}_0n^1 = {}_{83}Bi^{210}\,(RaE). \quad (3)$$

Another example, the artificially obtained ${}_{79}Au^{198}$ is likewise (Fig. 1) formed by the addition of a neutron to a «p-type» nucleus ${}_{79}Au^{197}$. Consequently, this artificial isotope of gold breaks the rule (1); therefore it is unstable and, being transformed to the permitted configuration ${}_{80}Hg^{198}$, emits β-rays ($T=2.7$ days).

II. It seemed of interest to trace the genealogy of heavy elements with the help of rule (1). We can see once more (Fig. 1) that those nuclei which

do not follow the rule (1) are β-active, while the nuclei that do follow it are resistant to β-decay, though liable to α-decay. This allows us to extend the above classification of stable nuclei (n, $2n$, p, a and α-type) to α-active isotopes as well. β-emitters are not classified here.

All heavy isotopes can be classed into five radioactive families which are called after their stable end-products, the Hg^{202}, Pb^{206}, Pb^{207}, Pb^{208} and Bi^{209}-families. The isotopes in Fig. 2—6 are denoted as in Fig. 1.



1. The Hg^{202}-Family (Fig. 2) consists of two radioactive branches «coadnate» at $_{84}Po^{214}$ (Rac'). One branch, consisting mainly of «a-type» nuclei, begins at $_{92}U^{238}$ and forms the so-called Uranium Disintegration Series. The other branch, which consisted of nuclei of «α-type», has already vanished. The unaccountable pleochroic halo-rings observed by Henderson and others [2] in uranium minerals are probably evidence of these vanished nuclei. Rings of the nucleus RaC' ($R_0 = 6.97$ cm) must, obviously, be found in such minerals more often than other rings.

As a result of α-decay, nuclei $_{84}Po^{214}$ transmute into $_{82}Pb^{210}$ (RaD). However, in spite of the universally adopted opinion, we cannot consider $_{82}Pb^{210}$ a β-emitter, since it does not break the rule (1) and can exist as a stable isotope [3]. As isotope 210 cannot be detected as a stable one among the

radio-lead isotopes ([4]), we must suspect it to be α-active. The next link of this chain, $_{80}Hg^{206}$, is not found among the stable mercury isotopes, and the disintegration chain is continued up to $_{80}Hg^{202}$. This last isotope is stable and is the most abundant of the mercury isotopes.

2. The Pb^{206}-Family (Fig. 3). The members of this family, $_{83}Bi^{210}$ (RaE) and $_{84}Po^{210}$ (RaF), are usually included in the so-called Long-lived Active Deposit of Radium. However, $_{84}Po^{210}$ can also be fed by the long-lived gas $_{86}Em^{214}$ which has not yet been found, being chemically indiscernible from its isotope $_{86}Em^{222}$ (EmRa).

3. The Pb^{207}-Family ascends at least to $_{92}U^{235}$ (AcU). This independent family (Fig. 4) consists mainly of «*n*-type» nuclei, but contains one α-active nucleus of «*p*-type», $_{91}Pa^{231}$. The radioactive chain coincides in general with the so-called Actinium Disintegration Series.

4. The Pb^{208}-Family (Fig. 5, *I*). The oldest ancestor of this family is $_{90}Th^{232}$, an «*a*-type» nucleus, while the other members of this family are «2*n*-type» nuclei. But it is possible that the pleochroic rings ($r = 5.9\,\mu$) observed by Henderson ([2]) in the biotite mica from Manitobe, belong to a still more ancient predecessor of this family ($_{92}U^{232}$ or $_{92}U^{236}$). This radioactive chain coincides in the main with the so-called Thorium Disintegration Series.

5. The Bi^{209}-Family is especially remarkable, as all its members, except the stable end-product $_{83}Bi^{209}$, have vanished (Fig. 5, *II*). Among the members of this family were the following isotopes of elements predicted so far back as by Mendeleyeff:

$$\left.\begin{array}{ll} Z = 85 & A = 213 \text{ and } 217 \\ Z = 87 & A = 221 \\ Z = 89 & A = 225 \end{array}\right\} \qquad (4)$$

As has recently been shown by Corson and Mackenzie ([5]), the element $Z = 85$ can be obtained by bombardment of bismuth with α-particles. This element is α-active (Fig. 1) and disintegrates with a period of $T = 7.5^h$.

Both Paneth ([6]) and M-lle Perey ([7]) have discovered α-activity in actinium. As may be seen from Fig. 1, the α-active isotope of actinium can be nothing else than the unknown isotope $_{89}Ac^{225}$.

III. It is known that Geiger-Nuttall's relation fails in the case of radioactive nuclei $_{92}U\,II^{234}$, $_{91}Pa^{231}$, $_{90}Th^{232}$ and $_{88}AcX^{223}$. But if we plot the logarithm of the disintegration constant as abscissa and the total α-decay energy in the 1/3 degree as ordinate, we obtain for each of the nuclear types a separate straight line (Fig. 6). In this figure the «*n*-type» nuclei are denoted by triangles; the «2*n*-type», by crosses, and «*a*-type» nuclei, by circles. The data, concerning the value of λ and E are taken from Bethe ([8]). The value of E for $_{90}Th^{232}$ is calculated according to the range ($R = 2.59$ cm) found by Henderson ([2]) (1937), taking into account the recoil energy. Data concerning U I, U II, AcU and Th are revised according to the new communication by Nier ([9]).

The graph shows that the straight lines for each of the nuclear types are not parallel. The slope to the ordinate axis gives the rate of the decrease in the lifetime of the radioactive nuclei as the kinetical energy of the α-particles inside the nucleus increases, i. e. it characterizes the penetrability of the barrier surrounding the nucleus of a given type.

As the minimum α-activity observed in the nuclei can be estimated by the period $T \approx 10^{12}$ years, the period $T \approx 10^{15}$ years ($\lambda = 10^{-23}$ sec.$^{-1}$) can be taken as a half-life of a practically stable nucleus. Thus, the empiric relation between the disintegration constant and the total energy of α-decay can be expressed analytically:

$$\lambda = \lambda_0 e^{-\frac{\sqrt{E-C}}{K}} \qquad (5)$$

where $\lambda_0 = 10^{-23}$ sec^{-1}.

The constant C is derived from the equation $C = \sqrt[3]{E_{min}}$, where E_{min} characterizes the minimum energy of α-particles still capable to leave the nucleus. In other words, $C^3 = E_{min}$ practically determines the depth of the potential pit of a given nucleus.

If, according to Bethe [8], we were to assume $T \approx 10^{-15}$ years ($\lambda = 10^{15}$ sec^{-1}) as the time of the life of a nucleus without a potential barrier, the height of the barrier would be derived from the equation

$$E_{max} = (K \ln 10^{38} + C)^3 M - v. \qquad (6)$$

Data, referring to the potential barriers surrounding nuclei of a given type, are summarized in Table 1.

Table 1

Nuclear type	Penetrability I/k $(M-v)^{-\frac{1}{3}}$	C $(M-v)^{\frac{1}{3}}$	Depth of pit $C^3 = E_{min}$ $(M-v)$	Height of barrier $h = E_{max}$ $(M-v)$
«n»	164 ± 1	1.598 ± 0.002	4.08	9.65
«a»	155 ± 3	1.518 ± 0.002	3.50	9.00
«$2n$»	145 ± 2	1.522 ± 0.003	3.53	9.56

The disintegration constants for RaC′, AcC′ and ThC′ and the total energy of α-decay of AcU, calculated after the formula (5), are summarized in Table 2.

Table 2

Nucleus	Nuclear-type	Total energy of α-decay E $(M-v)$	Disintegration constant (sec.$^{-1}$)
RaC′	«a»	7.83	$3 \times 10^{+6}$
ThC′	«$2n$»	8.95	$8 \times 10^{+10}$
AcC′	«n»	7.58	$1 \times 10^{+3}$
AcU	(«n»)	5.1	3.12×10^{-17}

The values λ and E ascribed to AcX (nucleus of «n-type») refer, probably, to some other nucleus, because the point corresponding to these values falls into the line of «$2n$-type». RaF, denoted by a square in Fig. 6, is the only α-active «α-type» nucleus (except the light nucleus $_{62}Sm^{148}$). Other nuclei of this type have disintegrated. The last representative of the «p-type» nuclei, $_{91}Pa^{231}$, is denoted by a cross in a circle. The rest of the nuclei of this type, being members of the extinct Bi-family, have vanished.

I thank S. I. Wawilow, Member of the Academy, for his constant interest in this work.

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TECHNICAL PHYSICS

CONTRIBUTION TO THE THEORY OF SYNCHRONIZATION OF RELAXATORY AUTOOSCILLATIONS

By K. THEODORCHIK

(Communicated by N. D. Papalexi, Member of the Academy, 28.IV. 1943)

The oscillation process in typical relaxatory autooscillation systems consists in an alternation of charges and discharges of the capacity; which range within two critical values of the potential V_1 and V_2. When either of these is attained, one of the processes becomes unstable and is superseded by the other process. Generally speaking; the growth and drop of the charge does not proceed always according to the same law.

Below we shall consider such relaxatory autooscillation systems in which the discharge is so rapid compared to the charge; that its duration may either be

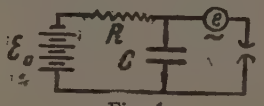

Fig. 1

altogether neglected or regarded as constant and independent of the external influences upon the system.

To take a concrete example we shall start with a relaxatory generator provided with a neon tube (Fig. 1).

The potentials at which the neon tube is lit and extinguished we denote by the symbols V_{20} and V_{10}, respectively. If the system is under a harmonic e. m. f. applied externally

$$e = e_0 \sin pt, \qquad (1)$$

the lighting and extinguishing of the tube may proceed at the potentials of the condensator equal to

$$V_{2,t} = V_{20} - e_0 \sin pt \quad \text{and} \quad V_{1,t} = V_{10} - e_0 \sin pt, \qquad (2)$$

respectively. The charging process obeys the equation

$$RCV + V = E_0$$

whence

$$t = RC \ln \frac{E_0}{E_0 - V}. \qquad (3)$$

From this the lighting and extinguishing moment are obtained by the substitution of the potential's critical values (2). For the period of autooscillations we get

$$\tau_1 = t_1 - t_0 + \theta = RC \ln \frac{E_0}{E_0 - V_{20} + e_0 \sin pt_1} + \theta - RC \ln \frac{E_0}{E_0 - V_{10} + e_0 \sin pt_0}. \quad (4)$$

Expressing time in angular measure

$$\psi = p\tau \text{ and } \alpha = p\theta \quad (5)$$

and introducing the values for the phase of the external force at the beginning and at the end of the period

$$\varphi_0 = pt_0 \text{ and } \varphi_1 = pt_1 + \alpha, \quad (6)$$

we obtain the following relations for the period and phases:

$$\psi_1 = pRC \ln \frac{E_0}{E_0 - V_{20} + e_0 \sin(\varphi_1 - \alpha)} + \alpha - pRC \ln \frac{E_0}{E_0 - V_{10} + e_0 \sin \varphi_0}, \quad (7)$$

$$\varphi_1 = \psi_1 + \varphi_0. \quad (8)$$

The subsequent periods are obtained in a similar manner. The final phase of the $(n-1)$-th period is apparently equal to the initial phase of the n-th period. For the sequence of values taken by the period and the phase we get the formulae:

$$\psi_n = pRC \ln \frac{E_0}{E_0 - V_{20} + e_0 \sin(\varphi_n - \alpha)} + \alpha - pRC \ln \frac{E_0}{E_0 - V_{10} + e_0 \sin \varphi_{n-1}} \quad (9)$$

$$\varphi_n = \psi_n + \varphi_{n-1}. \quad (10)$$

In an analogous way, for any system of the above-mentioned type when under the influence of an outward periodical (2π period) force $e = e(\varphi)$ we obtain

$$\psi_n = f_2\{R, C \ldots e(\varphi_n - \alpha)\} + \alpha - f_1\{R, C \ldots e(\varphi_{n-1})\} \quad (11)$$

$$\varphi_n = \psi_n + \varphi_{n-1}. \quad (12)$$

It may be seen from these formulae that autooscillations are no longer isochronous if some parameter determining the period is modulated by the external periodical influence. Then the duration of each period is uniquely determined by the phase value of the external force at the start of its application.

Isochronous autooscillations cannot possibly take place in the presence of an external periodical force unless

$$\varphi_n = \varphi_{n-1} = \varphi_0 \quad (13)$$

holds within $2\pi N$, i. e.

$$\psi = 2\pi N; \quad \tau = NT; \quad N = 1, 2, 3, \ldots \quad (14)$$

In other words, the occurrence of isochronous autooscillations under a periodical influence applied externally may only by observed on the condition that the autooscillations are synchronized by the external force.

We shall now prove that if in the absence of an external force the period of autooscillations ψ_0 is near enough to $2\pi N$, then, when the external force is present, the sequences ψ_n and φ_n will tend with increasing n to one of the above-mentioned synchronous regimes of order N, as a limit.

On the axes (φ, ψ) plot the functions

$$\psi_I = f_1\{R, C \ldots e(\varphi)\} \text{ and } \psi_{II} = f_2\{R, C \ldots e(\varphi - \alpha)\} + \alpha \quad (15)$$

each of which is a periodical function of a frequency which is either equal to or the multiple of the frequency of the external force. So the diagram of Fig. 2 can naturally be conceived as being built on the lateral surface of a circular cylinder.

It is easily seen that ψ_n may take no value beyond the totality of values run over by the projection on the coordinate axes of the intercept of the straight line drawn between the curves ψ_I and ψ_{II} at an angle of 45° to the φ-axis.

If the minimum and maximum values of this totality are such that

$$\psi_{min} \leqslant 2\pi N \leqslant \psi_{max}, \tag{16}$$

then a synchronization of order N is possible in the system.

In order to investigate the stability of a possible synchronous regime and the process by which it is established, let us build (Fig. 2) along with functions ψ_I and ψ_{II} one more function $\psi_I + 2\pi N$. The intersection points of the

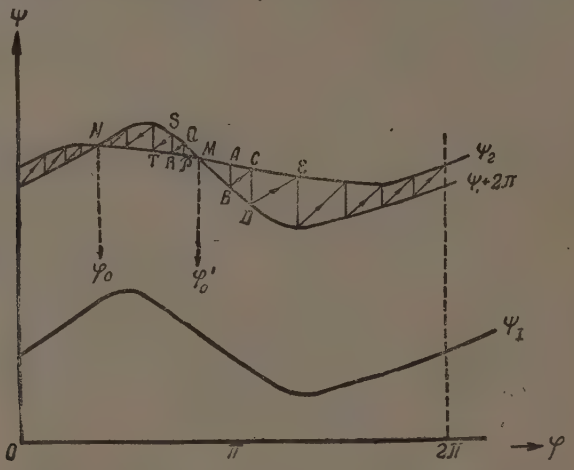

Fig. 2

curves $\psi_I + 2\pi N$ and ψ_{II} will evidently give the possible values of the synchronizing phase φ_0 ane φ_0'.

In the general case there may be $2n$ such values. One may readily verify that for any initial value of the phase the sequence of values φ_n as given by (11) and (12) can be found by drawing the broken lines

$$P \to Q \to R \to S \to T \to \ldots \to N,$$
$$A \to B \to C \to D \to E \to \ldots \to N.$$

This graph shows that the synchronizing value of the phase φ_0' is unstable, while the value of φ_0 is stable for any initial value of the phase. If the number of possible synchronizing values of the phase is equal to $2n$, then n of them are stable and the other n unstable, the stable and unstable values alternating along the φ-axis.

The intersection points, determining the synchronizing values of the phase, have as long the character of unstable and stable nodes represented in Fig. 2 as the inclination angle of the tangent to curves ψ as the point of synchrony remains less than 45°; or as long as

$$\left(\frac{d\psi}{d\varphi}\right)_0 < 1 \tag{17}$$

holds. As the depth of modulation of the curves ψ_I and ψ_{II} is proportional to the amplitude of the external influence, the condition (17) is always fulfilled in the case of feeble external influences.

The width of synchronization bands in that region increases monotonously with the amplitude of the external synchronizing force.

After a certain critical value is reached by the amplitude of the external force; the condition (17) breaks down. Then the stable value of the synchronizing phase is no longer stable; but rather assumes the character of an unstable focus or of an unstable node.

Moreover, the points of synchrony in that region may become unattainable for the system on account of the self-screening of a portion of the curve ψ_{II}.

Owing to this, the bands of stable synchrony in this second region grow narrower as the amplitude of the external influence increases; until they vanish altogether.

On the boundary of synchronization bands in the areas where the condition (17) is disturbed; there may take place a periodical convergence of the sequence of values assumed by the period.

By an analogous graphic representation it may be shown that the synchronization at the first undertone $N = \frac{1}{2}$ has the same character of periodical convergence for which

$$\lim_{n\to\infty} (\tau_{n-1} + \tau_n) = T. \tag{18}$$

All the above-said may be generalized to the case of an arbitrary relaxatory autooscillation system; if its corresponding system of equations (of the type (11); (12)) can be represented in the form

$$\psi_n = f(\varphi_{n-1}). \tag{19}$$

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GEOPHYSICS

RATIO BETWEEN SOLAR AND SCATTERED ILLUMINATION FOR CLOUDLESS SKY

By N. N. KALITIN

(Communicated by A. A. Grigoriev, Member of the Academy, 6.XI.1942)

Under conditions of a cloudless sky the illumination of an Earth surface situated horizontally is composed as a sum of illumination by the Sun (Lx) and illumination by the scattered light of the atsmosphere (lx); this sum is described as total illumination ($Lx+lx$). The magnitude of illumination by solar light depends upon the height of the Sun over the horizon; the transparency of the atmosphere and the distance between the Earth and the Sun. The greater the height of the Sun; the larger the value of Lx; Lx varies also directly with the transparency: the larger the coefficient of transparency of the atmosphere (p); the higher the value of Lx. The quantity lx varies with the height of the Sun in the same way as does Lx; i. e. it grows when the height of the Sun grows and diminishes as the Sun goes down. Not so with the relation between lx and p; lx varies inversely with p: the higher p, the lower lx.

As the albedo of the Earth surface increases; so does also lx; and conversely. On the other hand; Lx is not affected by the albedo at all.

It will be obvious that under natural conditions the ratio between Lx and lx is liable to strong variation.

It is the object of this work to trace the variation of this ratio in relation to the height of the Sun and to the albedo of the Earth surface (when covered or uncovered with snow) and with reference to observations under natural conditions. The effect of variations in the distance between the Earth and the Sun upon the illumination is no essential one; besides; it has no direct bearing upon the matter concerned. It is therefore left out of consideration in our reasoning.

The material of this investigation consisted of records taken for both kinds of illumination; obtained with the help of photoelectric recording photometers during three years at Slutzk; near Leningrad. For the analysis records were sorted out taken at completely cloudless days. These proved few in number, viz. 23. And as the magnitudes of illumination were measured every hour from sunrise to sunset, a total of 298 magnitudes has been obtained for altitudes of the Sun ranging from 0.5 to 52°.

These 23-day observations were divided into two groups: such as have been carried out without snow covering; and with it. The former consisted of 13 days embracing 204 measurements; the latter, 10 days with 94 measurements. The climatic and geographic conditions at the spot of observation prevented us from studying the influence of the albedo at Sun altitudes beyond 35°; since the snow covering does not withstand altitudes of the Sun greater than this, and melting takes place.

The relation between Lx and lx to be expected in a course of 24 hours is as follows. Before sunrise the total illumination of the Earth surface must be due to

scattered illumination alone. From the moment of sunrise, solar illumination is added to scattered illumination; and both illuminations will continuously increase in strength until midday. Solar illumination varies with the height of the Sun much more intensely; and the absolute magnitudes of *Lx* increase with the height of the Sun more strongly than those of *lx*; in the total illumination as measured within 24 hours it is *lx* that will prevail first; after a certain height of the Sun is reached; the amount of *Lx* will be equal to that of *lx*; and in the subsequent it is *Lx* that will be predominant. The same picture; though in the opposite direction; will take place between midday and sunset.

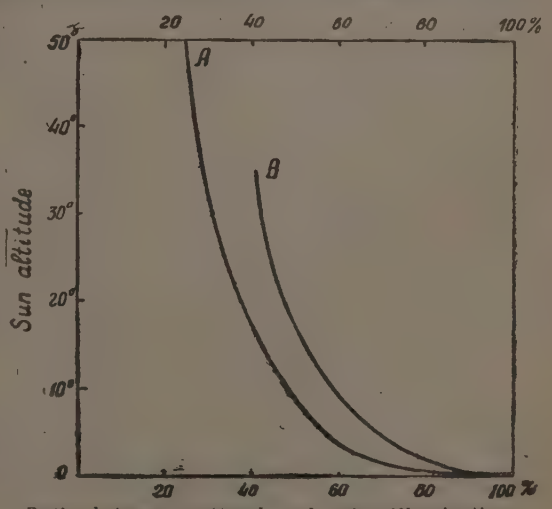
Average Magnitudes of the Solar and Scattered Illumination for Various Heights of the Sun above the Horizon
(in thousands of luxes)

Sun altitude	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
Without snow covering											
Lx	0	2.0	5.3	9.8	14.8	20.3	26.0	31.4	37.1	42.4	49.3
lx	0.5	3.2	5.3	7.1	8.5	9.6	10.5	11.3	12.1	12.7	13.2
With snow covering											
Lx	0	2.0	5.3	9.8	14.8	20.3	26.0				
lx	1.2	4.0	7.0	9.8	12.5	14.9	17.2				

The material treated enabled us to plot a table containing the average magnitudes for *Lx* and *lx*; both in the presence and in the absence of snow covering. From a graphic representation of these data it can be seen that in the absence of a snow covering; solar and scattered illumination become equal at an altitude of the Sun of 10° above the horizon.

In the case of snow covering the albedo must be greater; and so must be the magnitude of *lx*; consequently; the two illuminations must attain the state of equality at a greater altitude of the Sun. From the same graph the respective figure is found to be 15°.

As has been pointed out at the beginning of this article, we were interested in this work in the relation between *Lx* and *lx* at various altitudes of the Sun over the horizon; rather than in the absolute magnitudes of illumination.



Ratio between scattered and solar illumination for various Sun altitudes

As a result of a treatment of the material made under this angle; a figure has been plotted. Curve *A* of this figure gives the ratio of illumination due to scattered light of the atmosphere to total illumination in the absence of snow covering. Curve *B* illustrates the same ratio in the presence of a snow covering. The figure shows that in both cases the percentage of scattered radiation decreases continuously with increasing Sun height; while that of the solar radiation increases. This variation proceeds most intensely within the range from 0 to 7° of the Sun altitude.

When there is no snow covering and the Sun is at a height of 2° above the horizon, the scattered radiation makes up 65% of the total illumination; at a height of 30° it constitutes 30%, while at an altitude of 50° the figure is as low as 24%. The presence of a snow covering does not interfere with this relation; for the same Sun altitudes (2 and 30°) the per cent of scattered illumination makes up 80 and 41; respectively.

The conclusions arrived at in this study are not based on a very extensive material (in spite of the fact that the work was carried on during three years). It is therefore desirable that a similar study should be carried out on a more abundant material; and that the magnitudes of illumination be compared with the coefficient of the atmosphere transparency. It seems also expedient to choose for this work a more southerly region; which would permit to analyse the relation between the magnitudes of Lx and lx up to the highest possible Sun altitudes.

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CHEMISTRY

ABSORPTION SPECTRA OF AMIDO- AND AMINO-COMPLEXES OF BIVALENT PLATINUM

By A. V. BABAEVA

(Communicated by V. G. Chlopin, Member of the Academy, 16.II.1943)

The study of the absorption spectra of complex compounds of cobalt; chromium and nickel led the investigators to the conclusion that the absorption spectra of any complex compound comprise in the visible part of the ultra-violet up to 200 $m\mu$ three absorption bands. The appearance; position and intensity of these bands is determined by the nature of the central atom, by the nature of the inner sphere substituting atom and the spatial configuration of the complex. Nearly all the investigators; concerned with the absorption of light by complex compounds; agree that it is the second band in the absorption spectrum which is the main characteristic of complex compounds. Its appearance is due to the shattering of the bond: central atom—substituting atom; or even to the reversible dissociation of the latter. Accordingly, the energy carried by the rays of the frequencies of the second band can serve to measure the strength of the coordination bond. The liability of the substituting atom to deformation plays a considerable part in the localization of the absorption bands on the scale of the wave-lenghts. Substituting atom with a greater dipole moment must produce a greater effect on the displacement of the bands as compared with those having a smaller moment.

Ley (1), Inoüe (2), Johnson and Mead (3); Luther and Nikolopolos (4); Colmar and Schwartz (5) and others who investigated the absorption spectra of aqua- and amino-aqua complexes of nickel, chromium and cobalt, are unanimously asserting that the substitution of the amines in the inner sphere by water molecules leads to a shift of the two bands having the longer wave, and mainly of the first band, into the red end of the spectrum. The mass of ammonia and of water being almost equal, the frequency variation is due to the strength of the bond between this group and the central atom.

As shown by Samuel (6) and Mead (7), the nature of the amine tells but little on the position of the absorption bands. The difference is mainly manifest in the intensity, i. e. the magnitude of the molecular absorption index.

Such polar substituting groups as the halogens, the nitrogroup, the rodane group, oxalate and sulphate groups bring about more considerable spectral changes as compared with the neutral ones; viz. water, amines. In a number of papers the order of displacement of absorption bands towards the long-wave end of the spectrum is brought in relation with the nature of the substituting group; the so-called batochrome series:

NO_2, NH_3, OHO, H_2O, NCS, NO_3, SO_4, OH, C_2O_4, CO_3, Cl, CrO_4 Br, I.

In this series the largest shift towards the long-wave end of the spectrum is brought about by the presence of iodine in the complex; whereas the extreme

short-wave position of the band is due to the nitro-group. This series shows the above order for the first absorption band. For the second band the two first members of the series stand in an inverse order. According to Fajans ([8]) and to other authors;

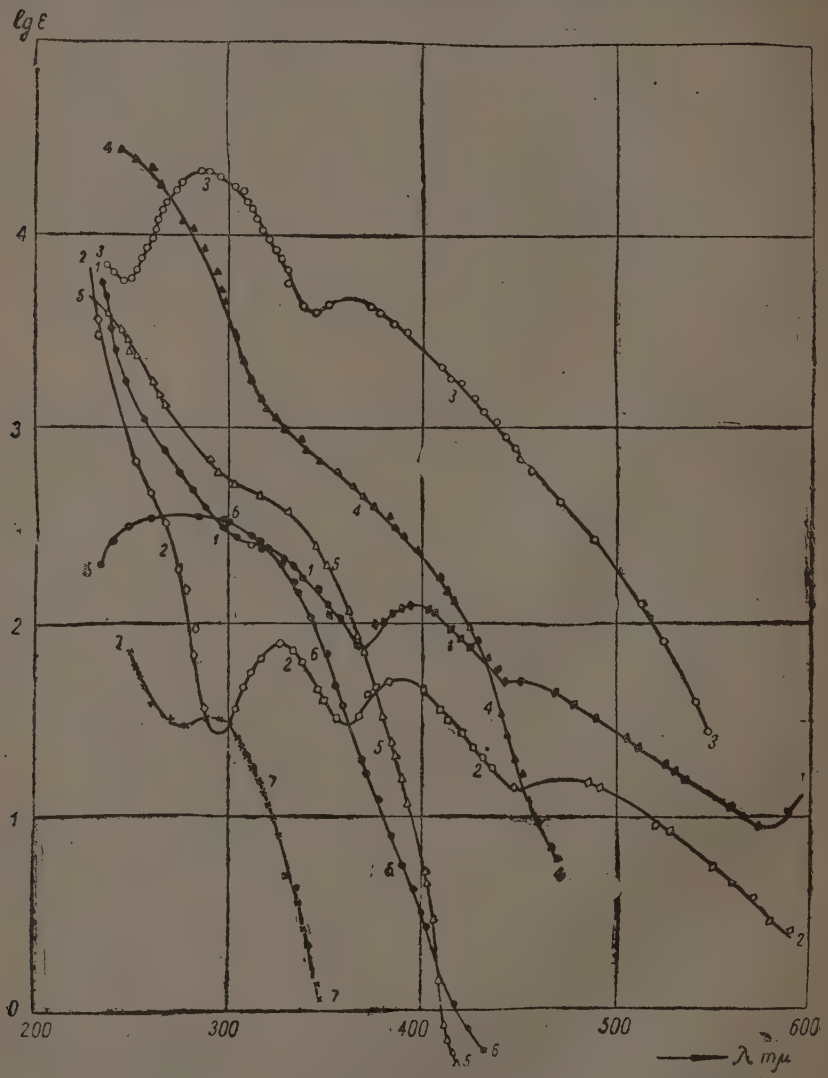

Fig. 1. *1*—$K_2[PtBr_4]$; *2*—$K_2[PtCl_4]$; *3*—$K_2[Pt(NCS)_4]$; *4*—$[Th_4Pt]Cl_2$; *5*—$K_2[Pt(NO_2)_4] \cdot 2H_2O$; *6*—$K_2[Pt(C_2O_4)_2] \cdot 2H_2O$; *7*—$[(NH_3)_4Pt]Cl_2 \cdot H_2O$

the influence of the nature of the substituting group upon the position of the absorption bands consists in the magnitude of its deformation by the central ion, which disturbs the electron symmetry and brings about a shift of the bands towards the red end of the spectrum.

The author has studied curves for the absorption of light in the region of wave lengths from 600 to 220 mμ of complex compounds of bivalent platinum, containing

in their inneir sphere the same acid or neutral substituting groups. The investigation was carried on with a Hilger quartz spectrograph (middle-size model) according to the method of Scheibe with the use of the rhomb of Hüfner and of the rotating spectrum. Freshly prepared aqueous solutions of complex compounds were used; the concentration being from 0.05 to 0.001 mol. In order to avoid hydrolysis to the solutions to be tested were added in the majority of cases small amounts of an electrolyte with an ion of the same symbol as that of the inner sphere substituting group.

Table 1

	λ_1, mμ	lg ε_1	λ_2, mμ	lg ε_2	λ_3, mμ	lg ε_3	λ_4, mμ	lg ε_4
1. K_2PtBr_4			450	1.68	395	2.11	(310)	(2.44)
. K_2PtCl_4	470	1.22	392	1.72	328	1.91	(260)	(2.80)
3. $K_2Pt(NCS)_4$			360	3.73	288	4.34		
4. $[Th_4Pt]Cl_2$			(320)	(2.84)				
5. $K_2[Pt(NO_2)_4]2H_2O$ . . .			313	2.66				
6. $K_2[Pt(C_2O_4)_2]2H_2O$ . . .			280	3.58				
7. $[(NH_3)_4Pt]Cl_2 . H_2O$ . . .			282	1.53				

In the case of potassium bromoplatinite three absorption bands have been found, but judging by the colour of this compound; another band should be expected in the visible region. Therefore; the band with a maximum at 450 mμ is the second absorption band. In the spectrum of potassium chloroplatinite there are three definitely expressed bands and a diffused one with a maximum about 260 mμ. On the light absorption curve it is expressed by a bent. A similar bent can be observed on the curve of potassium bromoplatinite.

The rhodanoplatinite $K_2Pt(NCS)_4$ is characterized by two absorption bands. The more short-wave band is probably due to the NCS′ ion, since the latter shows selective absorption at 270 mμ.

The thiourea compound $(Th_4Pt)Cl_2$ coloured yellow gives a curve of light absorption having no pronounced maxima. It consists of two branches of overlapping bands.

$$K_2Pt(C_2O_4)_2 \cdot 2H_2O,\ K_2Pt(NO_2)_4 \cdot 2H_2O \text{ and } [(NH_3)_4Pt]Cl_2 \cdot H_2O$$

give only one absorption band in their absorption spectra in the investigated interval of wave-lengths. If the energy carried by the rays corresponding to the frequencies of the second band is really spent on the loosening of the bond between the central atom and the substituting groups in the inner sphere and this band should be in the spectrum of every complex compound; their single band observed in the compounds mentioned must be the second band. This conclusion is supported by the order of the displacement of maxima along with the change in the inner sphere substituting group which has been described in earlier works. In fact, the introduction of the nitro-group into the complex brings forth in the case of cobalt and chromium compounds a shift of the maximum of the first band towards the short-wave end of the spectrum; and of the second one towards the long-wave end. Thus; the maximum of the second absorption band of $[Co(NH_3)_6]^{+++}$ is at 340 mμ and that of $[Co(NO_2)_6]^{---}$ at 358 mμ.

The shift of the maximum of the only band of the I Reiset base $[(NH_3)_4Pt]Cl_2.H_2O$ towards the long-wave end of the spectrum by 31 mμ when it is connected into $K_2[Pt(NO_2)_4] \cdot 2H_2O$ signifies that the only band in this area is the second band. The widening of the second absorption band in the case of $K_2[Pt(C_2O_4)_2]2H_2O$ should be explained by its merging with the band of the selective absorption of the $C_2O''_4$ ion. Potassium oxalate gives an absorption band at 260 mμ (7).

From Table 1 and from the curves it follows that the substitution of four chlorine atoms in the chloroplatinite by four nitro-groups; i. e. a conversion from $[PtCl_4]^{++}$ to $[Pt(NO_2)_4]^{--}$ sharply indicates the character of the absorption spectrum.

On the following series of compounds, investigated by the author, it is possible to follow the consecutive change of the structure of the curve of light absorption, when chlorine atoms in the chloroplatinite are gradually substituted by nitrogroups.

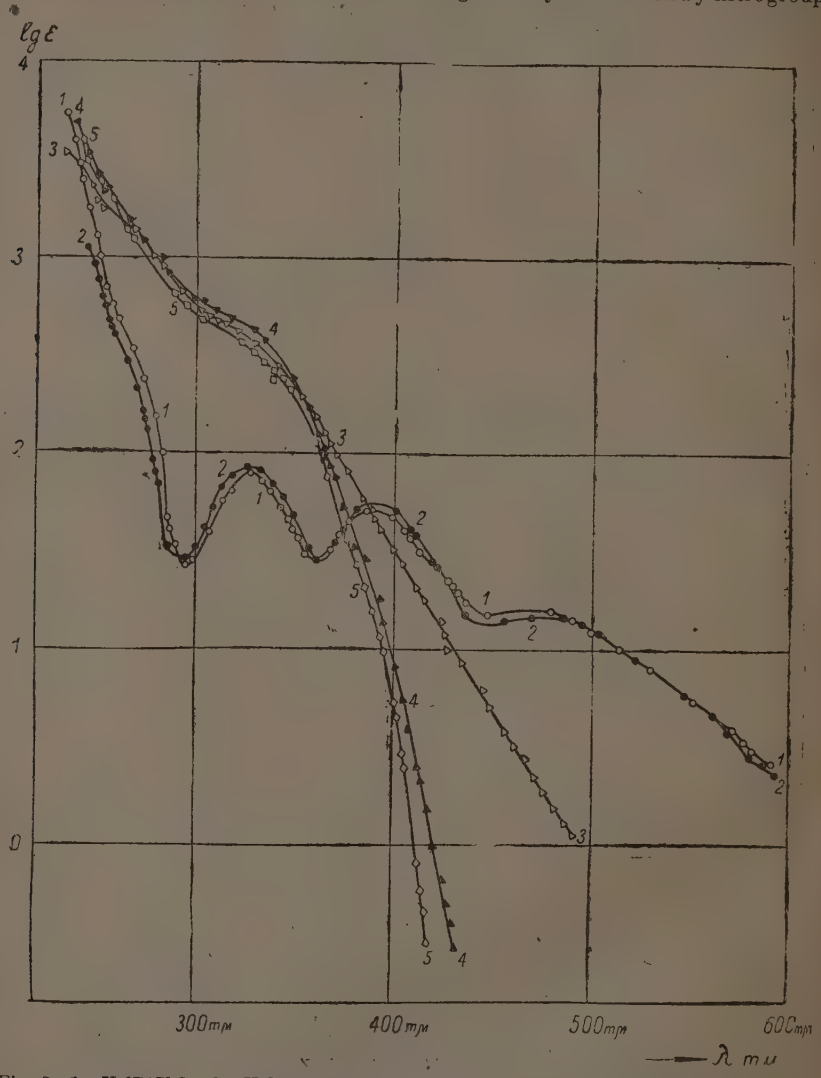

Fig. 2. *1*—$K_2[PtCl_4]$; *2*—$K_2[PtNO_2Cl_3]$; *3*—$K_2[Pt(NO_2)_2Cl_2]$; *4*—$K_2[Pt(NO_2)_3Cl]\cdot 2H_2O$; *5*—$K_2[Pt(NO_2)_4]\cdot 2H_2O$

It follows from Table 2 and from respective curves that the substitution of one chlorine atom by a nitro-group results in no change in the position of the absorption bands, but that the intruduction of the second nitro-group alters sharply the character of the whole spectrum. The first long-wave band disappears and the second one is shifted considerably towards the shorter-wave lengths. The third band becomes diffuse. The absorption coefficients increase considerably. Further increase in the number of nitro-groups in the inner sphere of the complex, i. e. a

Table 2

	λ_1, mμ	lg ε_1	λ_2, mμ	lg ε_2	λ_3, mμ	lg ε_3	λ_4, mμ	lg ε_4
1. K_2PtCl_4	470	1.22	392	1.72	328	1.91	(259)	(2.80)
2. $K_2PtNO_2Cl_3$	472	1.18	391	1.78	326	1.89	(260)	(2.58)
3. $K_2Pt(NO_2)_2Cl_2$			310	2.64	(260)	(3.20)		
4. $K_2[Pt(NO_2)_3Cl] \cdot 2H_2O$			315	2.70				
5. $K_2[Pt(NO_2)_4] \cdot 2H_2O$.			313	2.66				

transition to $K_2[Pt(NO_2)_3\ Cl]$ and to $K_2(Pt(NO_2)_4]$; brings about no essential changes in the absorption spectrum of these compounds as compared with the spectrum of $K_2\ [Pt(NO_2)_2\ Cl_2]$. The second and at the same time unique absorption spectrum of these complexes becomes narrower, but the position of the maximum scarcely undergoes any change. The slightly expressed rise near the maximum of the third band disappears. Thus, the presence of two or more nitro-groups in the inner sphere of the acidocomplexes of bivalent platinum makes the electron system of the compound stronger, and the energy of visible light and of the light in the near ultra-violet region is no longer insufficient in order to excite it.

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CHEMISTRY

SYNTHESIS OF AMMONIUM PHOSPHATES FROM FERROFERRIPHOSPHATES

By M. M. BYKOV

(Communicated by D. N. Prianishnikov, Member of the Academy, 12. III. 1943)

Ammonium phosphates are notoriously valuable as fertilizers rich in phosphorus and nitrogen. As the original raw material in their production calcium phosphates are generally used. But to obtain reactive phosphates of ammonium from the latter is a rather complicated affair. Phosphates of iron (collectively, vivianites used sometimes as fertilizers) have not yet been tried for the manufacture of ammonium phosphates.

According to A. E. Fersman (1), immense reserves of vivianite are stored in the biosphere. In White Russia they have been reported by Orlov (2) and other geologists to attain a figure of 750 thousand cubic metres (with P_2O_5 up to 17.5%). Vivianite beds occur also in Siberia.

Popov (3) gives formulae for the transition of vivianite $3FeO \cdot P_2O_5 \cdot 8H_2O$ into ferroferriphosphates: α; β; γ and oxykerchenites; $m\,FeO \cdot n\,Fe_2O_3 \cdot pP_2O_5 \cdot qH_2O$. I have made laboratory tests on the synthesis of ammonium phosphates and $FeSO_4 \cdot 7H_2O$ from synthetic β and oxykerchenites and from natural β-kerchenite, as well as from the products of their oxidation at 450—600° C. On natural oxidation of Kahlbaum's iron phosphate-2 at 0—25° for upwards of ten years I obtained a yellowish-green compound of the oxykerchenite type, but with RO = FeO. This was probably $FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 21H_2O$. Its analysis data (in %) are given in Table 1.

Table 1

	Kahlbaum's preparation	According to formula $FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 21H_2O$
FeO	6.00	4.69
Fe_2O_3	42.04	42.24
P_2O_5	28.22	28.12
H_2O	24.00	24.95
	100.26	100.00

Crystallooptical Data*. Constituent parts. 1) An isotropic substance with $N_m \sim 1.68$. Its content, 10—30%. 2) An anisotropic substance of a light-green colour in the form of needle-like crystals (elongated with

* All determinations have been made by M. P. Golovkov.

respect to N_g?); $N_p \sim 1.64$; $N_g \sim 1.70$. Content, 70—90%. From the oxidation of this compound and of the natural β-kerchenite at 600° C there arose a new substance, yellow-brown in colour, whose composition was probably $3Fe_2O_3 \cdot 2P_2O_5 = 4FePO_4 \cdot Fe_2O_3$. This presented isotropic colourless grains; 0.003 mm in diameter. The crystals were of the cubic system. Part of the grains had $n < 1.78$; the rest had $n > 1.78$ (there were also brown grains with $n > 1.78$; probably, $Fe_2O_3 \cdot n\,H_2O$). The composition of this substance is given in Table 2 (in %).

Table 2

	Test data	According to formula $3Fe_2O_3 \cdot 2P_2O_5$
Fe_2O_3	62.68	62.77
P_2O_5	37.15	37.23
	99.83	100.00

This appears to be the phosphorite anhydrite described by Popov ($3Fe_2O_3 \cdot 2P_2O_5 \cdot 17H_2O$). The synthesized compound seems to corroborate the general view expressed by Popov (3) relative to the oxidation of vivianites. I, however, am inclined to believe that in the case of synthetic phosphates the oxidation runs in one direction only, whereby our $FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 23H_2O$, like other kerchenites, is ultimately converted to phosphorite. Its formation I think to proceed according to the schemes:

$$4\{FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 21H_2O\} + O_2 = 6\{3Fe_2O_3 \cdot 2P_2O_5\} + 84H_2O \quad (1)$$

$$4\{5FeO \cdot 2Fe_2O_3 \cdot 3P_2O_5 \cdot 23H_2O\} + 5O_2 = 6\{3Fe_2O_3 \cdot 2P_2O_5\} + 92H_2O \quad (2)$$

and for the transition formula we have

$$4\{m\,FeO \cdot n\,Fe_2O_3 \cdot p\,P_2O_5 \cdot q\,H_2O\} + mO_2 = 2\{(m+2n)\,Fe_2O_3 \cdot 2p\,P_2O_5\} + 4q\,H_2O. \quad (3)$$

Qualitatively I have tested the action of HCl, H_2SO_4, H_3PO_4, HNO_3, $H_2C_2O_4$ on the described preparations. The action of $(NH_4)_2Sn$ on them has been studied in greater detail. In order to decompose the phosphates of iron 20 to 40-g portions were put in a glass container with ground-in stoppers and a stirrer. The rate of stirring the mixture was 160 revolutions per minute. The solutions $(NH_4)_2S - (NH_4)_2Sn$ were taken in 6 to 9 concentration, in triequivalent amounts (the sulphide of ammonium was prepared according to Tradewell-Hall; H_2S was obtained from commercial Na_2S or CaS). At 50° the decomposition of iron phosphates was practically complete in 6 hours (by a biequivalent ammount of $(NH_4)_2Sn$, as calculated for ammonia, 80—85% are decomposed). Iron sulphides and solid substances filter off from ammonium phosphate at 50°.

Starting from the data on solubility in water of $(NH_4)_3PO_4 \cdot 3H_2O$, as reported by Wolfkovich with associates (4) and by other authors (5), I saturated a warm filtrate with ammonia (at the end of saturation, at 0°). $(NH_4)_3PO_4 \cdot 3H_2O$ is filtered off and washed with a 50% NH_4OH. The yield of $(NH_4)_3PO_4 \cdot 3H_2O$ makes up 80—90% of the calculated. For these nearly isotropic crystals $(NH_4)_3PO_4 \cdot 3H_2O$ crystallooptic data have been obtained: $N_m = 1.500$; angle of optical axes (—) $2V$ large (?); birefringence ~ 0.007; extinction, straight; elongation, negative. In Table 3 analysis data (in %) for a pure $(NH_4)_3PO_4 \cdot 3H_2O$ are given.

The composition of the pure $(NH_4)_2HPO_4$ is given in Table 4 (in %).

$(NH_4)_3PO_4 \cdot 3H_2O$ and $(NH_4)_2HPO_4$ as obtained by us are nearly as pure as the standard reagents.

For commercial $(NH_4)_2HPO_4$ the analysis data are given in Table 5 (in %).

Table 3

Standard conditions as usually specified		Our preparation
Colourless crystals soluble in water		Same
Content of $(NH_4)_3PO_4 \cdot 3H_2O$ not under 95% .		P_2O_5 — 27.90 (according to other data 31.17) NH_3 — 21.36
Substances insoluble in water	0.005	0.028
Chlorides (Cl')	0.002	0.002
Sulphates (SO_4'')	0.022	0.037
Ferrum ($Fe^{\cdot\cdot\cdot}$)	0.001	0.0005
Heavy metals	0.001	0.0005
Nitrates (NO_3')	0.0005	0.0005
Alkaline metals	—	0.68
Arsenic (AsO_4''')	0.0005	0.0005

From its components, the substance synthesized is likely to be a useful fertilizer. This conclusion, however, should be verified by the results of its introduction under different farm crops.

Table 4

Substances insoluble in water	not above		0.019
Chlorides (Cl')	»	»	0.002
Nitrates (NO_3')	»	»	0.0005
Sulphur (total)	»	»	0.016
Alkaline metals (in the form of phosphates)	»	»	0.82
Iron ($Fe^{\cdot\cdot\cdot}$)	»	»	0.0005
Heavy metals	»	»	0.002
Arsenic (AsO_4'')	»	»	0.001
P_2O_5	»	»	55.56
NH_3	»	»	24.96
The reaction of water solution (1/10 *M*) pH = 7.8 .	»	»	

The by-products of the reaction are also of importance. Upon the neutralization of the filtrate [from $(NH_4)_3PO_4 \cdot 3H_2O$]HCl with hydrochloric acid NH_4Cl and S are formed. From NH_4Cl ammonia is extracted. FeS and Fe_2S_3 are decomposed by a 4*n* solution of H_2SO_4, and from the solution S and $FeSO_4 \cdot 7H_2O$ (with an admixture of $MnSO_4 \cdot 7H_2O$) are extracted. The content of $FeSO_4 \cdot 7H_2O$ in a preparation once recrystallized is up to 88%, and that of MnO, 0.13%. After 3 recrystallizations the respective figures are 90—92 and 0.065. This may be said to be a commercial product of a rather high degree of purity. By calcining the iron sulphide I obtained iron oxides and SO_2.

Table 5

Found		According to formula $(NH_4)_2HPO_4$
P_2O_5	53.35	53.76
NH_3	24.89	25.83
Iron ($Fe^{\cdot\cdot\cdot}$)	0.0005	
SO_4'' and S . . .	0.95	
Arsenic (AsO_4''') . .	0.001	
Humine substances .	0.22	
Reaction of water solution (1/10 *M*) pH=7.9		
Hygroscopicity . . .	1.9	

$(NH_4)_3PO_4 \cdot 3H_2O$ like the idiochromatic compounds, ferroferriphosphates, show a poor stability. The use of the latter for the extraction of ammonium phosphates as fertilizers and reagents, along with the by-products of the reaction, is of certain interest, the more so as this domain has not yet been investigated.

The presence of $(NH_4)_3PO_4 \cdot 3H_2O$ was proved by analysis; but FeS and Fe_2S_3 were not easy to analyse. The series rule of Tananaev [7] gave us a certain hint, but in the case of our system it has a limited application. Accord-

ing to Mecklenburg and Rodt [8], Fe_2S_3 is isomerised to $FeS \cdot FeS_2$, aud accordind to Feigl and Bäcker [9], Fe_2S_3 is significant for two isomeric forms: $S:Fe \cdot S \cdot Fe:S$ and $FeS \cdot FeS_2$, which is connected with the pH of the medium. With pH greater than 7 there is no isomerization. If $(NH_4)_2Sn$ is applied, isomerization is observed because NH_3 passes off in vapour. All this makes it difficult to appreciate the character of the reaction, the more so because the decomposition of the phosphate by S″ and Sn″-iones does not come to completion. We have the fundamental simple formulae:

$$3FeO \cdot P_2O_5 \cdot 8H_2O + 3(NH_4)_2S = 3FeS + 2(NH_4)_3PO_4 \cdot 3H_2O + 2H_2O \quad (4)$$

$$5FeO \cdot 2Fe_2O_3 \cdot 3P_2O_5 \cdot 23H_2O + 11(NH_4)_2S = 5FeS + 2Fe_2S_3 + 6(NH_4)_3PO_4 \cdot 3H_2O + 4NH_4OH + 3H_2O \quad (5)$$

$$FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 21H_2O + 13(NH_4)_2S = FeS + 4Fe_2S_3 + 6(NH_4)_3PO_4 \cdot 3H_2O + 3H_2O + 8NH_4OH \quad (6)$$

$$3Fe_2O_3 \cdot 2P_2O_5 + 9(NH_4)_2S + 15H_2O = 3Fe_2S_3 + 6NH_4OH + 4(NH_4)_3PO \cdot 3H_2O. \quad (7)$$

For the decomposition of the natural β-kerchenite (Schelkovo, Moscow province, and from White Russia) we have:

$$\underset{\text{solid phase}}{5FeO \cdot 2Fe_2O_3 \cdot 3P_2O_5 \cdot 23H_2O} + \underset{\text{liquid phase}}{11(NH_4)_2S} = \underset{\text{solid phase}}{5FeS + 2Fe_2S_3} + \underset{\text{solid} \rightleftarrows \text{liquid phase}}{6(NH_4)_3PO_4 \cdot 3H_2O} + \underset{\text{liquid phase}}{4NH_4OH + 3H_2O} + \underset{\text{solid} + \text{liquid phase}}{\text{humine substances} + \text{solid solution.}} \quad (8)$$

The presence of FeS was established according to Stokes [10] and from the reaction $FeS + PbSO_4 = PbS + FeSO_4$ upon heating (the ions of $Fe^{\cdot\cdot\cdot}$ were few). Fe_2S_3 was determined according to Stokes at 170° (no $Fe^{\cdot\cdot}$ was detected in the filtrate), and from the reaction with ammoniac $CdSO_4$ [9]. When phosphates containing $(NH_4)_2Sn$ were acted upon by Fe^{+2}, an oxidation process for the Fe^{+2} atoms was observed, which accords with Stokes' data [10] on $Fe^{\cdot\cdot}$ ions in solution.

To sum up, there has been proved the possibility of using a new raw material — iron phosphates — for the production of ammonium phosphates as fertilizers or reagents, and also of by-products. The method proposed here solves the problem of utilizing all iron phosphates and heavy metals. The procedure is simple, does not require a long time and involves only generally accessible reagents.

Two new compounds have been synthesized: $FeO \cdot 4Fe_2O_3 \cdot 3P_2O_5 \cdot 21H_2O$ and $3Fe_2O_3 \cdot 2P_2O_5$. For them and also for $(NH_4)_3PO_4 \cdot 3H_2O$ crystallooptic data have been obtained.

The most valuable advices of D. N. Prianishnikov and A. E. Fersman, of the Academy, and of Prof. N. A. Tananaev and Prof. S. I. Wolfkovich are here greatfully acknowledged.

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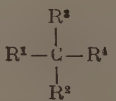
CHEMISTRY

CONTRIBUTION TO THE PROBLEM OF THE SYNTHESIS OF PARAFFINS COMPRISING A QUATERNARY CARBON ATOM THROUGH ZINC ALKYLS

By A. L. LIBERMAN, M. G. LUKINA, O. P. SOLOVOVA and B. A. KAZANSKY

(Communicated by S. S. Nametkin, Member of the Academy, 12. III. 1943)

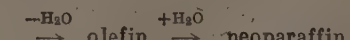
Syntheses of neoparaffins

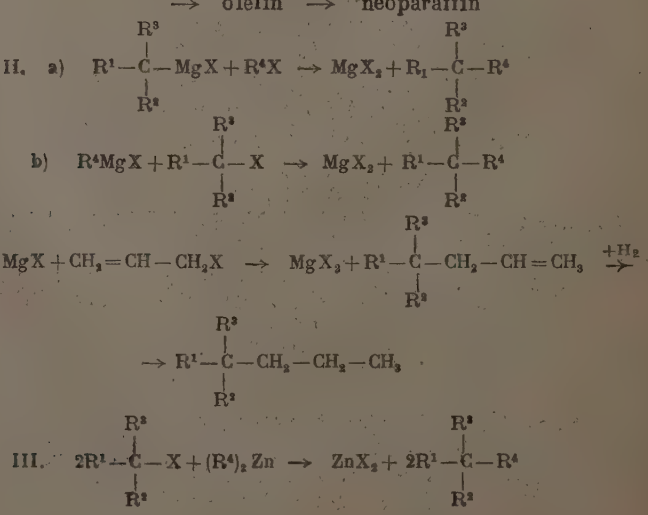


are very intricate. The methods of their preparation, as described in the literature; are very complicated; they lead in most cases to low yields and do not always guarantee that the hydrocarbon to be obtained is quite individual.

The three following schemes of the syntheses of neoparaffins are most widely employed:

I. Alcohol comprising a quaternary carbon atom





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Scheme I has a grave defect; since dehydration of the alcohols comprising a quaternary carbon atom is attended with a considerable risk of isomerization, and consequently; with a formation of mixtures of the isomers; the separation of which may be quite embarrassing; as observed by many authors([1]). Nevertheless; some authors succeeded in preparing individual neoparaffins in agreement with this scheme by dehydrating the alcohols by Tschugaeff's method ([2]); or by pyrolysis of the acetates ([3]).

According to scheme II; the neoparaffins may either be obtained directly (II; a,b), but in very low yields (10 to 20%) ([4]); or through an intermediate stage of olefins (II; c) ([5]). In the latter case; any β-unsaturated alkyl halide which is not liable to suffer allylic rearrangement; as for instance allyl chloride or bromide; serves as the second component in the Grignard-Würtz synthesis. The olefins and; consequently; the paraffins are obtained hereby in an extraordinary pure state and in satisfactory yields. Nevertheless; its use is somewhat restricted by the fact that the second component is usually a halide with three carbon atoms; or; in other words, only such neoparaffins may be prepared in this way which comprise a radical, consisting of a chain of three carbon atoms linked with the quaternary carbon atom. Besides; on account of the tedious and cumbersome procedure; the synthesis is inconvenient when the neoparaffins are to be obtained in considerable quantity. However; all its value holds as a method of preparing in individual state of the olefins with a quarternary carbon atom; which are hardly attainable otherwise.

Considerable interest belongs to scheme III. This method; the difficulty whereof is usually somewhat exaggerated; besides giving the possibility of introducing various radicals into the prepared neoparaffins; opens the way for carrying out synthesis on a large scale; as shown by Howard ([6]); who obtained 600 to 700 ml of 2; 2; 4; 4-tetramethylpentane in one charge by acting with zinc dimethyl upon 2; 2; 4-trimethyl-4-chloropentane. Synthetizing neoparaffins in agreement with the scheme III; Noller ([7]) introduced an improvement into the method of preparing zinc dialkyls; acting upon the copper zinc couple with a mixture of alkyl bromide and iodide; instead of pure iodide with which the reaction proceeds too violently. It has been found that in this case the alkyl bromides were the first: whereas the iodides only second to be consumed. According to Noller's assumption; this singular phenomenon proceeds according to the scheme:

$$RI + Zn \rightarrow RZnI$$
$$RZnI + RBr \rightarrow RZnBr + RI.$$

The alkyl iodide thus recovered may interact with zinc once more. Such a scheme of «catalytic» effect of alkyl iodides accounts for the fact that alkyl bromides readily interact with zinc under Noller's conditions; whereas in the pure state they do not interact with it at all.

The most conspicuous defect of this method is the fact that the paraffins obtained require special purification; since it follows from Noller's paper, as well as from the observations made by the present authors while repeating his synthesis, that the parrafins obtained boiled within 1 or 2 degrees. Purification of the obtained neoparaffins was effected by the authors by prolonged shaking with conc. sulphuric acid at room temperature and by subsequent fractionation on a precision rectification column with an efficiency of 23 theoretical plates. Hydrocarbons with the following properties have thus been obtained.

3, 3-Dimethylpenthane from tertiary amyl chloride and zinc diethyl: b. p. 85.4° (748 mm); $n_D^{20} = 1.3912$; $d_4^{20} = 0.6936$; $MR_D = 34.34$ (calcd. for C_7H_{16} $MR_D = 34.53$).

3-Methyl-3-ethylpenthane from tertiary hexyl chloride and zinc diethyl: b. p. 117.2° (750 mm); $n_D^{20} = 1.4082$; $d_4^{20} = 0.7274$; $MR_D = 38.77$ (calcd. for C_8H_{18} $MR = 39.14$).

The second drawback of Noller's method is the fact that when neoparaffins with eight or more carbon atoms are wanted; iodides with four or more carbon atoms must be used and; therefore, prepared, thus making the synthesis more compli-

cated and expensive. In order to avoid this inconvenience; the authors decided to substitute the higher alkyl iodide with the easily available ethyl iodide. In fact; if Noller's assumption were valid; the mixture of the higher alkyl bromide with ethyl iodide would interact with the copper-zinc couple according to the scheme:

$$C_2H_5I + Zn \rightarrow C_2H_5ZnI$$
$$C_2H_5ZnI + RBr \rightarrow RZnBr + C_2H_5I.$$

After both alkyl halides had been completely consumed; a mixture of zinc dialkyls is prepared from the reaction mass; by interaction with the tertiary alkyl chloride this mixture should yield two neoparaffins with dissimilar number of carbon atoms. These neoparaffins may easily be separated by fractional distillation. Our conjecture has been tested on the example of synthesis of 2; 2-dimethylhexane. The mixtures of zinc dialkyls prepared from butyl bromide and ethyl iodide taken in the molar ratio of 3 : 1; or from butyl bromide; ethyl bromide and ethyl iodide taken in the molar ratio of 3 : 3 : 2; respectively, have been brought into contact with tertiary butyl chloride; Noller's procedure having been followed in all other respects. In both cases a mixture of 2; 2-dimethylbutane and 2; 2-dimethylhexane has been obtained; which could be easily separated by fractionation. The hydrocarbons had the following properties:

2, 2-Dimethylbutane: b. p. 49.05—49.25° (748 mm); $n_D^{20} = 1.3696$; $d_4^{20} = 0.6510$; $MR_D = 29.89$ (calcd. for C_6H_{14} $MR_D = 29.91$).

2, 2-Dimethylhexane: b. p. 105.6—105.9° (743 mm); $n_D^{20} = 1.3941$; $d_4^{20} = 0.6962$; $MR_D = 39.23$ (calcd. for C_8H_{18} $MR_D = 39.14$).

The formation of 2; 2-dimethylhexane under the conditions described above may to a certain degree be regarded as a confirmation of the mechanism advanced by Noller; viz. that zinc alkyls are formed from alkyl bromides in the presence of iodides as a result of the «catalytic» effect of the latter.

Conclusions. 1. Among the most usual schemes of synthesis of neoparaffins the interaction of a tertiary alkylmagnesium halide with allyl halide (with subsequent hydrogenation of the olefin) and the interaction of tertiary alkyl halide with zinc dialkyl are the most expedient.

2. The latter method may be improved by using zinc dialkyls prepared from a mixture of alkyl bromides and iodides whose hydrocarbon chain differs by 2 or 3 carbon atoms. A mixture of two hydrocarbons is obtained; which are readily separated by fractionation. Data are obtained in favour of the inducing rôle of alkyl iodides during the interaction of zinc with alkyl bromides.

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CHEMISTRY

INVESTIGATION IN THE GROUP OF VITAMIN K. MECHANISM OF THE BIOLOGICAL ACTION OF VITAMIN K AND OF ITS SYNTHETIC ANALOGUES*

By M. M. SHEMIAKIN, L. A. SHCHUKINA and G. B. SHVETZOV

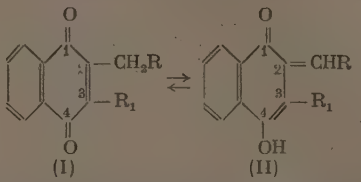
(Communicated by S. S. Nametkin, Member of the Academy, 20.II.1943)

A large number of investigations has been devoted to the study of the relationship existing between the structure and the biological effect of compounds belonging to the group of vitamin K. But in spite of a considerable accumulation of experimental data neither the regularities observed; nor the mechanism of the biological effect of natural vitamins K_1 and K_2 and of their numerous synthetic analogues have so far been interpreted in a satisfactory way. As early as 1939 L. F. Fieser put forward a hypothesis ([1]); which he further evolved in 1941 ([2]). According to it, the biological activity of the majority of analogues of vitamin K is not a direct action, but is rather due to their conversion in the organism; through biosynthesis, into quinones of the type of natural vitamin K. The problem of the mechanism of the biological action of the latter remained and still remains unsolved. The hypothesis of Fieser does not conform to some of the available experimental data; gives no adequate interpretation to many more of them, and is decidedly in contradiction with the fact that phtalic acid ([3]) was found to have an unmistakable; although very feeble; antihaemorrhagic activity; and that; according to recent observations, its diethyl ester is highly active (biological tests carried out by B. A. Kudriashov). It is, indeed, hardly probable that phtalic acid or its derivatives could be biologically converted into compounds of the series of 1; 4-naphthaquinone.

These observations gave a certain foundation to the hypothesis that the natural vitamins K_1 and K_2 and their synthetic analogues should be considered only as provitamins, and that the antihaemorrhagic activity of all these compounds is due to their oxidative cleavage to phtalic acid; the latter being the true carrier of their biological functions. A particularly weighty confirmation of this hypothesis are our observations; made quite recently; on the capacity of such highly active analogues of vitamin K as 2-methyl-1; 4-naphthaquinone and potassium 2-methyl-1, 4-naphthaquinone-3-sulphonate to be converted extremely easily into phtalic acid, already when simply heated with water; thus; under conditions that can be easily set up in the organism. A detailed study of the chemism of these transformations and of other properties of quinones related to the group of vitamin K; undertaken thereupon, make it possible for us to draw the conclusion that the biological activity of the natural vitamins K_1 and K_2; as well as of all their analogues; related to the derivatives of the naphthalene series; is actually a consequence of their capacity to be converted into phtalic acid; and that the relationship existing bet-

* Report at the session of the All-Union Institute of Experimental Medicine, in Moscow, December 5, 1942.

ween the structure of their molecules and the degree of their biological activity comes mainly to the influence of the one or the other structural factor upon processes leading to the formation of phtalic acid. The possibility of the natural vitamins K_1 and K_2 and of their analogues of being converted into the latter and; hence; their biological activity can be expressed; according to our point of view; only in the case when there becomes possible the appearance of the tautomeric system (I) $\rightleftarrows$ (II), which at the same time is an oxidation-reduction system:



(I) (II)

(R_1, hydrogen atom or hydrocarbon radical; R_1, hydrogen atom, hydrocarbon radical or any other group of atoms); in which the quinone (I) plays the part of the oxidizing agent * and is converted into the hydroquinone or into products of further changes of the latter; and the enol (II) plays the part of the reducing agent-being eventually oxidized into phtalic acid**.

Thus; the possibility of the appearance of biological activity depends; first of all, on the possibility of the appearance of the tautomeric system (I) $\rightleftarrows$ (II) and of a series of subsequent oxidation-reduction processes. The influence of structural factors upon the biological activity is confined mainly to their influence upon these transformations.

In this light the regularities established experimentally between structure and biological activity in the group of vitamin K are not in contradiction with the expressed opinions; but; on the contrary; support them. At the same time the regularities have found a proper explanation.

In more detail the results of our investigation will be reported elsewhere.

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* It is possible that in the organism the part of oxydizing agent can be assumed by other compounds as well.

** Taking as an example potassium 2-methyl-1,4-naphthaquinone-3-sulphonate, we have been able not only to isolate both tautomeric forms, that have been obtained as the corresponding potassium derivatives, but to prove experimentally that such a tautomeric system is actually at the same time an oxidation-reduction system, having demonstrated the oxidation of the quinoid form to the corresponding quinhydrone and the oxidation of the enol form to phtalic acid.

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GEOLOGY

KARST PHENOMENA IN THE KAZAN AREA OF THE VOLGA REGION

By S. G. KASHTANOV

(Communicated by V. A. Obruchev, Member of the Academy, 18.VII.1942)

On the territory of this Union karst phenomena are of wide occurrence; they are found in association with very different geological formations: Devonian (province of Leningrad), Carboniferous (of Moscow and Tula); Permian (along the western slope of the Urals); Jurassic (Crimea); Cretaceous (Caucasus and province of Voronezh); and Tertiary.

The karst owes its formation to the joint action of underground and aboveground waters. The activity of these waters is connected with the processes of dissolution of rocks; such as gypsum; anhydrites; limestones and dolomites.

In the Volga region about Kazan the karst is spread rather widely and mainly in the vicinity of a gypsum anhydrite stratum dating from the Lower Permian. In the structure of the described region Upper Carboniferous; Permian and Quaternary formations take part. The most ancient of them; i. e. the Upper Carboniferous and the Permian; compose the bed of erosion depressions which are filled with more recent sedimentary rocks.

The karst forms occur mainly along the left bank of the Volga from the town Zeleny Dol; where they meet with the Mari karst zone; close to the mouth of the Kama river; within the limits of the first and the second terrace overlaying the flood plain. Here V. N. Sementovsky separates 6 main groups: Zeleny Dol; Karavaevo; Derbyshkino; Shcherbakovo; Devlikeyevo; and Stolbishchy ([1]). The essential feature of karst is the formation of sink-holes. The holes can be ring-shaped; conical; cup-like and saucer-like. The ring-shaped holes have steep; nearly vertical walls. They are 60 to 80 m deep; or more. Compared to the depth, their width is rarely considerable. They are seldom encountered; and are discovered only by drilling. The conical holes are usually 6—12 m deep, occasionally 33 to 38, and 2 to 22 m in diameter; sometimes 37 or even 120 m. The cup-like holes are more shallow; their depth ranges from $2^1/_2$ to 7 m; and rarely attains 11 m. They are 10 to 40, sometimes 53 to 68 m wide. The saucer-like holes are flat; not above 1—2 m in depth, occasionally they are 4—$4^1/_2$ m deep and 25—48 m wide. The holes increase in size where the Quaternary cover grows in thickness, in other words, the largest holes are associated with the second terrace above the flood plain. The conical holes are filled with water and form lakes (Raifskoe; Glubokoe; Goluboe and others). This is sometimes also the case with saucer-like holes. Part of the karst lakes are fed by snow and rain waters; and then they contain fresh water which is used by the population (village M. Kabany; Proval, Sabakayka; etc.). Other lakes receive their water from Permian deposits. This water is as hard as to reach 60—70 German degrees (Shcherbakovo lakes). The ascending springs appear to originate in the Lower Permian water-bearing horizons and are emptied into the lake Goluboe. Some of the lakes by virtue of hydraulic forces are connected with the near-by basins through a system of fissures.

It seems that the karst zone continues along the left bank of the Volga and below the mouth of the Kama in the Alexeyevsk and Kuybyshev districts of Tartary (Three Lakes, Bezdna-Zateevka, Proval on the Kama; etc.).

The Volga karst is connected with the destruction and leaching out of Permian rocks. In the district of Zeleny Dol M. S. Kaveyev links up the karst zone with the Upper Kazan formations. According to V. N. Scmentovsky; the karst of Volga is mainly Kungurian. The accumulation of data secured by drilling corroborates this view. Thus, in course of a geological survey for railway building near vil. Kuyuki a well was sunk in a saucer-like hole amidst Quaternary sand-clay deposits, which encountered abundant fragments of Kazan-stage rocks and at a depth of above 80 m opened up the country rocks—an anhydrite stratum belonging to the Lower Permian. The prospecting well No. 1 in the vicinity of the village Verkhny Uslon at a—27 m mark discovered fragments of limestones of the Lower Kazan substage; whereas their base in the country bed lies at a mark of+20 m. Here the destruction zone of the gypsum anhydrite stratum at some places attains a mark of —60 m. Similar data; that the bottom is likely to sink down to gypsum-anhydrite stratum of the Lower Permian; or of the lowermost portions of the Lower Kazan; were secured by the wells put at the vicinity of Kazan; Verkhny Uslon; Zeleny Dol and in the region of the mouth of the Kama river.

From the drilling data available the following conclusions may be drawn. The Lower Kazan substage does not appear to give rise to karst; or, in other words, is composed by rocks not liable to karst formation. In the Upper Kazan deposits readily soluble rocks (gypsum) are encountered in the form of caverns; buds; or small lenses amidst limestones and dolomites. Their leaching-out leads to the formation of small empty spaces and small fissures, the latter being sometimes filled with fine sand.

The Lower Permian deposits are represented by gypsums; anhydrites; limestones and dolomites; which are mainly readily soluble rocks.

In some of the wells of the Near-Kazan region (Kuyuki; Verkhny Uslon) broken down anhydrites and dolomites have been discovered in the upper portions of the gypsum-anhydrite dolomite stratum. The rocks lying farther down are dense; solid; without any sign of leaching-out or fissure formation. This circumstance cannot but stand in definite relation to an excessive sinking of the bottom of the ancient valley of the Volga; and to the influence of this sinking on the regime of karst-waters. In the valley of the Kama bore-holes of the water power-plant of Kuybyshev discovered excessive sinking of the Neogenic valley of the Kama in a number of points (Chelny; Elabuga; Sokolki; Betky; Smylovka). In these points a 100 m thick layer of dark-gray clays; alternating with loams of a similar colour and with yellow fine-grained sands, have been encountered by the well beneath Mindel-Riss sands. Fauna is rarely met with in these deposits and has a fresh-water character. Shells of *Dreissensia*; *Bythinia*; *Unio* and others have been found in them. One of the wells in the region of Kamsky Poliany cut across fresh-water deposits down to the mark of—105 m of absolute height which is 150 m lower than the surface of the modern valley; and it yet failed to reach their base. In village Betky the erosion surface of country rocks attains a—100 m mark. Judging by the marks, these formations lie beneath the deposits of Akchagyl, including *Cardium* and *Mactra*. For that reason A. V. Mirtova believes them to belong to fresh-water analogues of the Lower Pliocene formations (1). There is, however, some isolated evidence that fresh-water deposits overlie Akchagyl and, consequently, are of a younger age and may be synchronized with the Domashkino horizon of A. P. Pavlov and A. N. Mazarovich.

The fresh-water stratum overlies now the Ufa, now the Artinskian formations. In the roof of the latter accumulations of breccia-like rocks, 8—12 m thick, have not infrequently been discovered; they are due to karst formation in these regions.

The geological profiles cutting across the valley of the Kazan-Volga region point to the existence of two erosion valleys (Zeleny Dol, Kazan, Kamskoe Ustie): a western valley, which is more shallow and in which runs the

modern bed of the Volga; and an eastern, deeper, valley, filled with more ancient deposits. The more ancient valley in the town Kazan is filled with a thick layer of fresh-water dark clays, containing poorly preserved shells of *Dreissensia* and carbonized plant remains.

The well No. 642 of the Drilling trust (Burtrest) sunk 1940 in the vicinity of Kazan, south-west of village Savino, after having attained a depth of 130 m did not traverse the whole thickness of Neogen clays all the same, and was stopped at a—52 m mark. It is a matter for regret that no one of the deep wells has here hit the middle of the ancient valley of the Volga. The latter (a Neogen valley) has been cut into as deep as the country rock and reached the Lower Permian (Kazan, Kamskoe Ustie, Zeleny Dol). Thus, in the continental Pre-Akchagyl epoch vast and deep valleys were prepared, which later served as routes for the transgression of the Akchagyl sea, which reached the lower courses of the Kama and the Kazan-Volga region. This may be interpreted to mean that the whole territory which had been considerably elevated in the Pre-Levantine times sank during this latter period. In the subsequent time the old valleys served as bed[illegible] river-streams of the Glacial epochs.

Within the territory of the Ma[illegible] Autonomous SSR the excessively deep valley of the Volga has never been reached by wells, but its existence here in previous times leaves no room for doubt. Very likely it formed a continuation of the valley of the Vetluga which; in turn; through the upper courses of the rivers Pijma and Vai; continued a river flowing farther north along the western border of the Mari-Viatka.

So it will be obvious that there was a time in the history of the Volga and Kama when the bases of erosion lay 100 m and more lower than to-day. It is possible that the water-table was accordingly deep. The presence of a deep valley along the course of the Volga created favourable conditions for the erosion of Lower Permian rocks as early as in the Neogen. At the same time the vertical movement of ground waters extended to a much greater depth than it does to-day; and reached the surface of the Lower Permian gypsum-anhydrite-dolomite stratum. During this period of intense circulation of ground water in Lower Kazan formations and in the upper portions of Lower Permian formations an energetic leaching-out of rocks was taking place. Naturally enough; the gypsum-anhydrite-dolomite stratum was the most affected by the process of dissolution; which fact accounts for the vast scale of the karst formation in the Lower Permian.

Simultaneously; and partly during the subsequent time; the ground waters in the upperlying Upper Kazan deposits likewise were leaching away the easily soluble rocks and worked themselves out vertical ways of movement. Into these holes; pipes and fissures a clastic material from the overlying Quaternary alluvial deposits was later on washed-in from the surface. Having come across a similar phenomenon in the district of Zeleny Dol; M. Kaveyev attempted to account for the formation of karst along river banks entirely by the percolation of fine clastic Quaternary rocks into small cavities of the Upper Kazan substage rocks. As a result of the penetration of fine clastic materials into cavities; the formation of small holes is indeed possible; but; as may be seen from what has been said above, they are only of secondary importance.

During the Quaternary the process of karst formation was subject to gradual extinction; and the small sink-holes which appeared during the recent time at some places (Kazan; Zeleny Dol) are only echoes of the ancient karst.

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GEOLOGY

SOME NOTES ON LOESS

By A. N. SOKOLOVSKY, Member of the Academy of Sciences of the Ukrainian SSR

Within these 25 years the problem of loess became from a purely theoretical problem one of the most important problems for hydrotechnical and civil engineering.

In spite of the presence of copious geological; petrographic; geographic, pedological and recently botanical works; our knowledge of loess as a natural body remains yet insufficient. The most essential points concerning the behaviour of loesses are not yet elucidated, in so far as they are connected with the properties of its solid phase surface. These properties depend not only on the composition of the cations adsorbed; but also upon the character of the surface layer of the «anion» part of the colloidal micella.

The question as to the degree of saturation of loesses with $\ddot{Ca}$ has always attracted great attention on the part of soil scientists (K. K. Gedroiz; A. N. Sokolovsky, A. F. Tulin; I. N. Antipov-Karatajev and others); it is now successfully applied in geology and lithology of sedimentary rocks; too (A. D. Arkhangelsky; L. I. Pustovalov and others).

As early as in 1919 the author showed that in each type of soil there is inherent a type of variation of the values of cation adsorption along the profile and of the whole behaviour of the soil colloids; as well as of distribution through the profile.

The author proposed the adsorption of NH_4^+ from a $0.1n$ NH_4Cl solution as a conventional criterion for the adsorptive capacity of soil. Its degree of saturation with Ca can be determined not only by the usual methods; but also by the ratio $\frac{A}{K}$ or $\frac{A-K}{A} \cdot 100$; where A are the adsorption values of NH_4^+, and K; adsorption of $\ddot{Ca}$ (m-eq.); supposing that the adsorption of the latter is inversely proportional to the degree of saturation of the colloidal (adsorbing) complex.

This method permits of a rapid determination of relative indexes of saturation with calcium even in the case of calcareous soils and deposits; which is otherwise impossible.

By means of this method the maximum saturation (87—95%) in profiles of zonal soils has been shown to refer to the horizons of chernozems and podsolized chernozems (especially to those; directly overlying calcareous illuvium). The degree of saturation of soils decreases northward and southward to the chernozem zone, in the former case owing to podsolization; and in the latter; to the alkalinization process.

From the theoretical standpoint the value of the saturation coefficient must be positive in all cases; and the ratio $A : K$ greater than 1. As a matter of fact; it was found that the process of alkalinization (and partly of podsolization) provokes in the adsorbing complex such fundamental changes that the relative affinity to $\ddot{Ca}$ increases extremely; the ratio $A : K$ becomes less than 1 and the coefficient of

saturation takes a negative value ($-n \cdot 100\%$); dropping as low as—457% in the crusty solonetz.

Some interesting variations are shown by the adsorbing (colloidal) complex of loess and the ordinary chernozem formed on it.

Exchange Cations in Ordinary Poltava Chernozem

Horizons		Exchange cations m.-eq. %. (in 5.4 *n* extracts of NH_4Cl)					Adsorption m.-eq. %		Degree of saturation,%	
		Ca	Mg	K	Na	Total	NH_4	$Ca^{..}$	Found	Calcd
H (A_1)	0—8 cm	34.1	6.2	0.8	1.8	42.9	11.1	1.3	79.5	88.3
K/P (*B/C*)	72— 80	18.8	5.8	0.7	0.9	26.2	10.4	2.15	71.8	79.7
P (*C*)	220—228	11.2	6.2	0.6	1.7	29.7	12.0	6.7	38.0	44.2

minus the Ca from carbonates

It may be seen that the course of variations of the saturation values along the profile; as determined from the formula and actually found in the case of partial displacement; are in very good agreement.

The first thing to point out is the significant lagging of the base exchange as compared to the adsorption downwards along the profile, and secondly; it is a much greater absolute and relative decrease of exchange Ca in loess. The first may be explained only by the fact that the adsorbed $H^{\cdot}$ which in this case is only an antagonist of $Ca^{..}$; could not be taken into account. Both these phenomena are quite unexpected in calcareous deposits (in the horizon *P*(*C*)—10.5% $CaCO_3$).

At the same time the behaviour of this loess when treated in succession with a 5.4 *n* solutions of NH_4Cl confirms the above stated; if we take in consideration the solubility of $CaCO_3$ in NH_4Cl, we get a negative value for the exchange Ca; in other words; the loess reacts vigorously with the dissolved carbonate. This should be taken to mean that during the whole period of existence of loess the conditions necessary for a complete interaction between the colloidal (alumosilicate) and carbonate compounds were absent.

Various degrees of saturation for other loesses of the Ukraine were found: in the steppe south-east from Poltava at a depth of 178 cm it makes up 53.5 and at 248 cm 36.4% (for the horizon 0—9 cm; 77.2% and for the horizon 42—51 cm; 87.6%); the loess-like deposit with small boulders at 630 cm has given 27.8%; and loess without boulders at 420 cm; 84.8%. Various values of saturation were found in the outcrop 10 m deep on the right bank of the river Orel near Rjasske; viz. from—52.8% (same as in solonetz soil) and 30.8 to 79.3%. The samples of loess from the Andijan experimental station at a depth from 1 to 5 m have also decreasing values (66.7; 64.8; 63.2%).

The upper part of the loess deposits under the gray and dark-gray forest loam of Dikanka showed a high degree of saturation, 90—96%; contrary to the steppe loesses. The difference between the steppe and forest regions is due to the presence of «dead horizons» (of G. N. Vysotzky) in the former and the absence of them in the latter; where the loess stratum has been subjected to the action of solutions with high content of Ca-ion. Hence the high degree of saturation.

The above-said led the author to the conclusion (1919) that the typical loesses have been deposited and existed during a long time under conditions of a dry climate.

These peculiarities of the typical loess; as well as its high porosity (sometimes above 50%); make us disavow the hypothesis as to its aqueous origin, since, first, water deposits of stagnant water (e. g. loams) have a low porosity and, secondly, in case they are not alkalized, they offer all conditions for a complete interaction between the solution of Ca-hydrocarbonate with their colloidal part; hence to a full saturation with $Ca^{..}$.

At the same time the «soil theory» of L. S. Berg [2], postulating the transformation of any rock of adequate composition into loess under the influence of «loess-forming» power; loses any foundation; since when loess is deposited in dry climate; there were no conditions necessary for the loess-forming process; i. e. no «sufficient content of a soil solution in the presence of carbonates» (S. S. Neustrujev)[4].

In this case it is not only the lack of moisture, but also of CO_2 which; connected with the scarcity of organic residues in semi-desert or desert conditions, prevents the mobilization of carbonates. Besides; the «soil theory» does not agree with the existing ideas as to the stratigraphical and genetic correlations between the soil and soil-forming rocks.

Thus; the peculiar features of the loess discovered by the author may be explained only from the standpoint of the aeolian hypothesis.

But then a question arises: wherefrom has been brought by the wind the loess material whose primary property; besides high porosity and high $CaCO_3$ content, is the low degree of saturation with Ca; and where such properties may be realized in nature. This question may be answered; owing to our knowledge of soil-forming processes and of soil geography: such a material is yielded by the solonetz soil-forming process; developing under conditions of dry climate and poor vegetation and resulting in a sharp differentiation of the profile. Deflation of the upper horizon of solonetz; possessing a loose structure, and of the alkaline soils of Middle Asia, Kazakhstan, Caspian depression and other, smaller, areas, has given the material for the loess dust.

At the same time acquires special importance the idea of Tutkovski [7] to the effect that winds from glacier turned clockwise to the west; developing this idea, Krokos [3] wrote that the loess dust has been brought from Eastern Russia. Of special interest is the hypothesis of Obruchev [5; 6] about a strong «current (draught) of air»; blowing from the east along the corridor formed between the margin of the glacier and the southern mountain systems (Alps; Carpathians; Caucasus) and bringing the dust from the Aralo-Kaspian plains onto the southern steppes. Development and repeated renewal of the alkalinization process were favoured by climate variations and epeirogenesis; in so far as these influenced the hydrological and hydrogeological regime of soil formation. As an evidence of these processes may serve the vast regions of crusty and columnar solonetz soils; as well as of takyr soils with an extremely reduced; sometimes absolutely absent eluvial horizon $EH(A_1)$.

Thus, the soil process really played a prominent part in loess formation, but in the places of formation of loess material rather than in the regions of its deposition. The determination of the degree of saturation with $Ca^{\cdot\cdot}$ of loesses and loess-like deposits can help in diagnosticating the genesis of loesses; as well as of their liability to subsidence.

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ON THE STRUCTURE OF PERICARP IN WHEAT KERNEL

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Aside from the high economical importance of cereals; their fruit; or kernel; being a very peculiar formation from the morphological point of view, is a subject of great theoretical interest. A huge endosperm; to whose lower part a well developed embryo is closely pressed; an extremely thin seed-coat which in some cases is totally lacking; and a sufficiently thin; soft pericarp, closely adhering to the seed-coat; all of this lends to the fruit of cereals such an aspect and properties as are encountered in no other plant.

So far the cereal kernel has received no proper characteristic in a precise formula which would reflect the morphological essence of the fruit. Considerable difficulties in the way of understanding the morphological nature of the kernel as a fruit arise partly from the fact that up to the present no detailed differentiation of structural peculiarities of kernels have been made; according to the different tribes of the family *Gramineae*; which not seldom exhibit striking differences in their morphology. Thus; the kernels of rice and sorgo; of barley and maize have so different a structure; that one is reluctant to refer them to the same category of fruit. In rice; indeed; its pericarp and its seed-coat are united into a single formation hard to separate; which is a very delicate formation at that. But this is hardly true of the integuments of the kernel in sorgo. And while the furrow is well expressed in barley; it is absent in maize. In hulled barley and in certain varieties of rice a ripe kernel is entirely deprived of a seed-coat which is resorbed in the process of ripening, leaving the seed naked. Generally speaking; the early and strong depression of textural integrity of the integuments, when the seed-coat is formed out of them; has the consequence that in most of the types of cereal kernel the function of the seed-coat is assumed by the pericarp. The functional versatility of the pericarp is the most forcibly expressed in the period of grain ripening.

In face of the great economic importance of the pericarp of cereals (for instance, in milling industry); our knowledge concerning it is far from being complete; but is rather confined to most primitive conceptions based on studies made a very long time ago and in no methodical manner. They failed therefore to disclose the great variety of structure in pericarp from different parts of the kernel. The object of the present investigation was to show; by taking wheat as an example; how diversified this structure really is.

At the moment of fertilization the pericarp of the young kernel has the same structure throughout. Its tissue consists of roundish parenchymal cells; containing starch grains and plastides along with the protoplasm and the nucleus. The fertilization almost immediately begins sharply to change the structure of the pericarp. The fruit grows very rapidly, the contents of the pericarp cells is resorbed, and many of the cells vanish. In a ripe fruit 20 to 25 layers of ovary wall-cells leave occasionally only one layer of cells that have preserved their structure; and the rest is

a structureless thin membrane. However; the metamorphosis of the pericarp structure does not proceed in the same way in all part of the kernel; but rather varies with the physiological requirements of the particular part of the fruit and the peculiarities of its growth in the different periods of development. Although every fruit presents a harmonic whole; which is especially true of monosperms; nevertheless, the endosperm develops under somewhat different conditions from the embryo. In cereals the endosperm has many characters which separate it very sharply from the embryo. The furrow with its vascular system is connected with physiological processes of a different nature as compared to those with which the back is connected; where there is no special conducting system. Certainly; the differences in the physiological features of a particular region should run parallel with structural differences. The structure faithfully reflects the processes taking place in the organism.

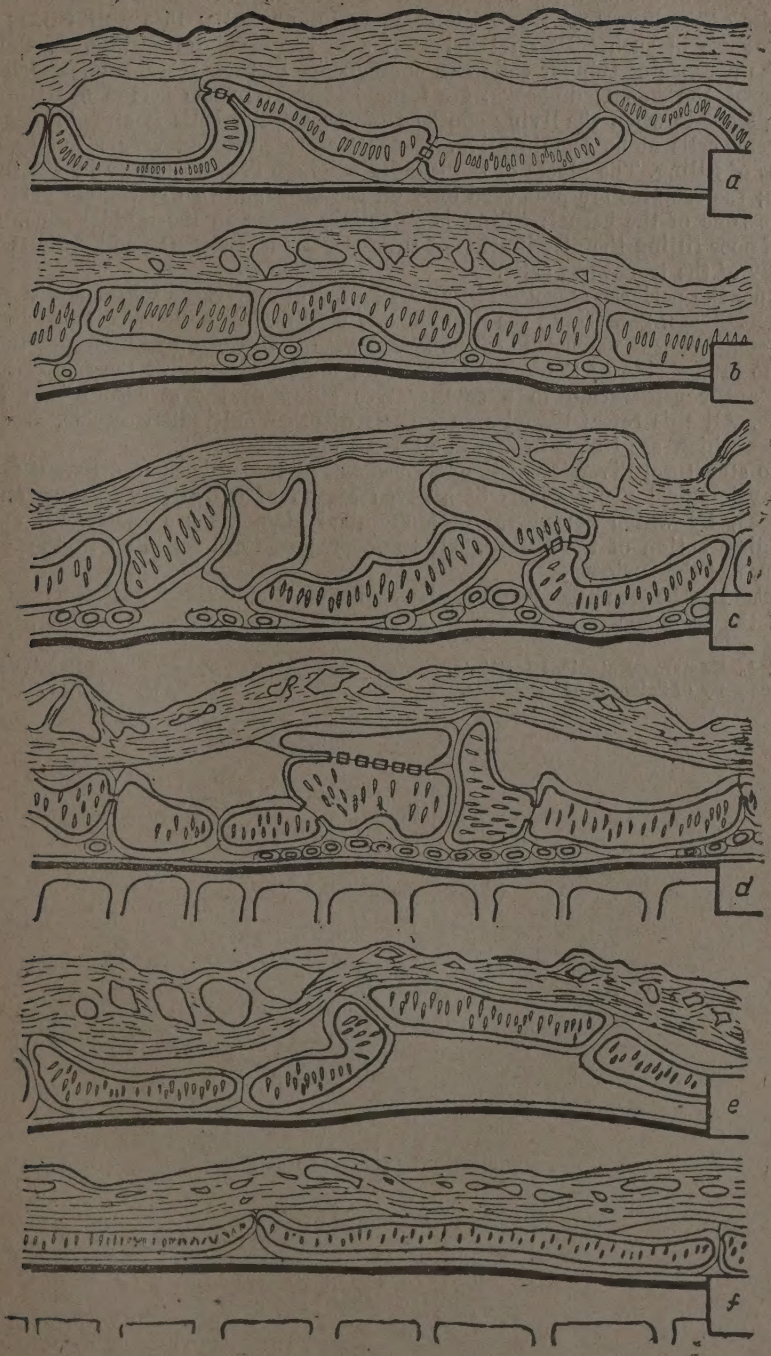
In the present paper the variety of the pericarp structure in different portions of a ripe fruit of *Triticum compactum* Host. is demonstrated on 6 fragments combined in 2 sections. The first section composed of 4 fragments (*a; b; c; d*) shows the conditions of the structure of the integument in the ridge of the back of a kernel along its length; the second section composed of two fragments (*e, f*) presents the lateral part of the middle portion of the kernel. All of the fragments are cross-sections through the integument of the same fruit; presented under the same magnification.

The integuments consist of pericarp and of seed-coat (spermoderm). In order to make out the peculiarities of structure in the seed-coat; a special treatment of the preparation is necessary; we represent it in the form of two stripes; a white and a black one located between the peripheral layer of the endosperm (aleuron layer) and the pericarp. We shall concentrate our attention on the pericarp alone. In the pericarp of a fully ripe kernel of *Triticum compactum* only one row of peculiacells; transverse cells; is distinctly visible everywhere. The epicarp with the remains of the mesocarp form a continuous; nearly structureless membrane of the epi-mesocarp. The endocarp is far from being present everywhere. In the compact wheat form under consideration it is found only on the back.

The back in a kernel is the quietest place of the fruit; it is scarcely affected by the tension exerted on the integument by the process of filling; when the endospermal tissue is extended from within; owing to the enhanced accumulation in it of newly formed starch grains. Fragment *a* is the part of the pericarp situated on the ridge of the back in the upper portion of the kernel. Since the living contents of the tranverse cells are the last to die away among the cells of the pericarp, the time of their active growth is longer. The result of this additional growth is that the cells are bent in different directions. The transverse cells and the membrane of epi-mesocarp; on the one side; and the seed-coat; on the other; comprise large cavities filled with air. Near towards the middle of the grain (fragment *b*) the transverse cells make a somewhat different growth than they do in the apical portion and gain here noticeably in width. In the middle of the grain the remains of the endocarp are visible in the form of dispersed tubular cells of a roundish shape.

About the embryo itself (fragment *c*) some of the transverse cells become nearly isodiametrical in form; and the tubular cells gain in number. Over the embryo (fragment *d*) the transverse cells look like typical parenchymal cells which were given the opportunity to grow more or less freely. At some places the tubular cells form a close tissue consisting of a single layer.

The structure of the pericarp in a wheat kernel is greatly dependent not only upon the place where the particular portion of the pericarp is located; but to a considerable extent also on the conditions of growth in the respective region. The distending influence of the growing endosperm is seen with particular clearness on the lateral sides of the fruit (fragments *e; f*). We shall here only show the cross-section of the middle portion of the kernel: upper fragment *e* is the portion of pericarp not far away from the ridge of the back; lower fragment *f* is the lateral side. Comparisons of the structure of pericarp in the middle of the grain, the ridge of the back (fragment *b*) with its state in other parts of the same cross-section


a
b
c
d
e
f

(fragments e and f), made in the light of the history of development of the fruit; reveal a variety of factors by which the peculiarities of structure are determined. On the ridge of the back the tubular cells are preserved. Somewhat nearer towards the sides of the kernel we find no longer any tubular cells; in a well filling grain the presence of such cells on the lateral side is indeed impossible. In the first case the absence of tubular cells is a consequence of their resorption. The sides of the kernel, the so-called cheeks, are formed (bulge) in the period of filling. The filling steps-in when the living contents of the tubular cells is already dead; the transverse cells alone remain alive. The latter are stretched very strongly in the process of filling. The places of the tubular cells are drawn asunder by the bulging cheeks; the remains are preserved only on the back and in the ventral part of the middle zone of the kernel; filling is especially strong in the middle zone. In the case of poor filling the distribution of tubular cells is different; and so is the morphology of the transverse cells.

Thus, the pericarp structure in a ripe kernel of cultivated wheat is different in different places. Sometimes the difference is very essential. This becomes apparent while comparing the structure of the apical with that of the basal part, or the back and the lateral side of the kernel. Therefore the topography of the fruit is a very important consideration in a comparative study of the structure in different kernels. All this refers likewise to kernels of other cultivated cereals; especially to those which are liable to more or less strong filling.

The structural diversity of the pericarp can be traced back to different reasons: the physiological peculiarities of a given region of a fruit; lysigenous enzymic processes, by which complexes of anatomical elements are destroyed; and the distending action of the filling. All these processes are reflected in the peculiar structure of the pericarp.

Virtually the structure itself is also a process, one of the manifestations of the life of the organism.

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